New Li-B-N-H Quaternary Hydrides

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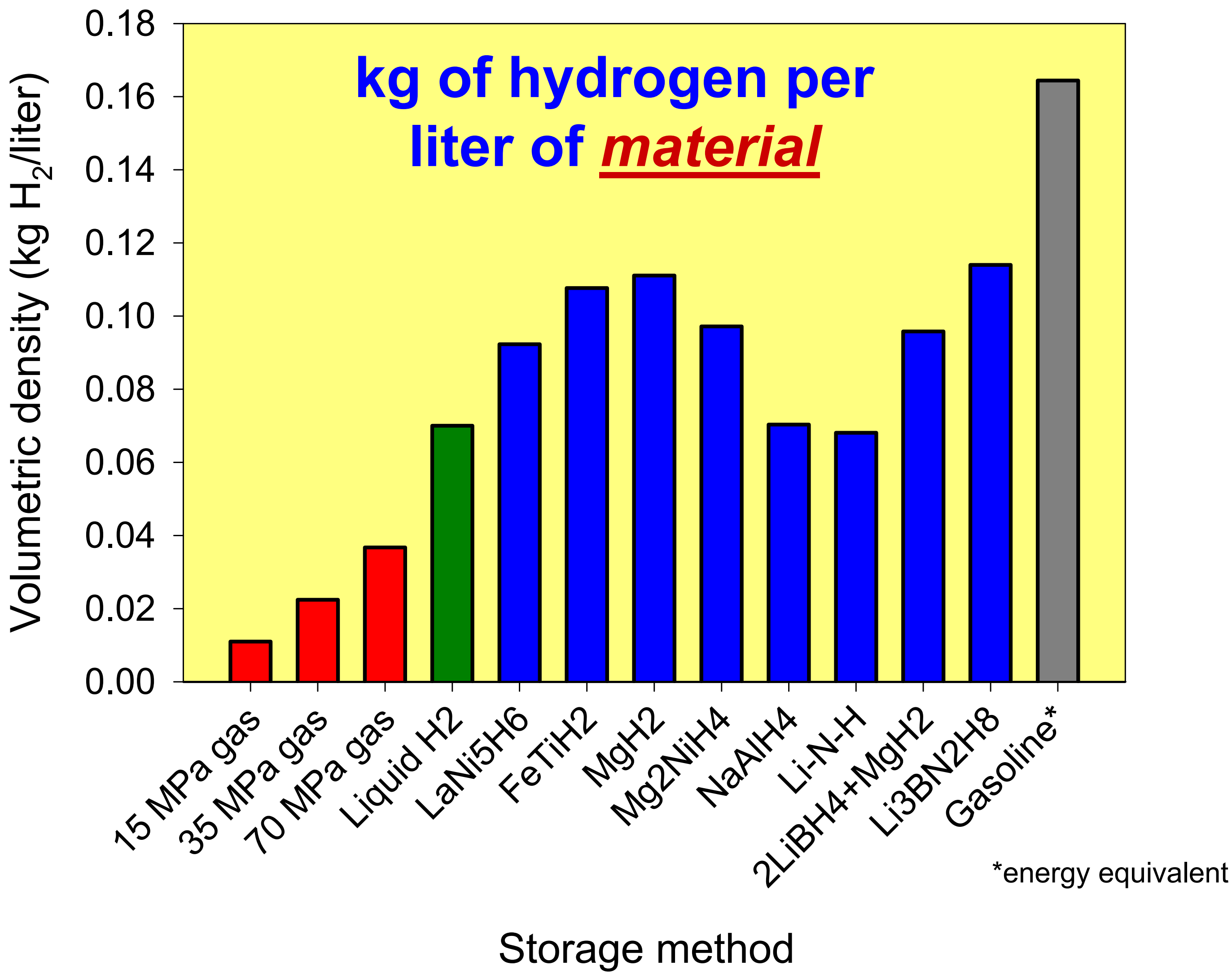
Outline

- Hydrogen storage requirements for solid hydrides
- Building high hydrogen capacity storage reactions
- New quaternary Li-B-N-H hydride
  - Synthesis from $LiNH_2$ and $LiBH_4$
  - Hydrogen release properties
  - Crystal structure
- Metal additives to promote hydrogen release
- Concluding remarks

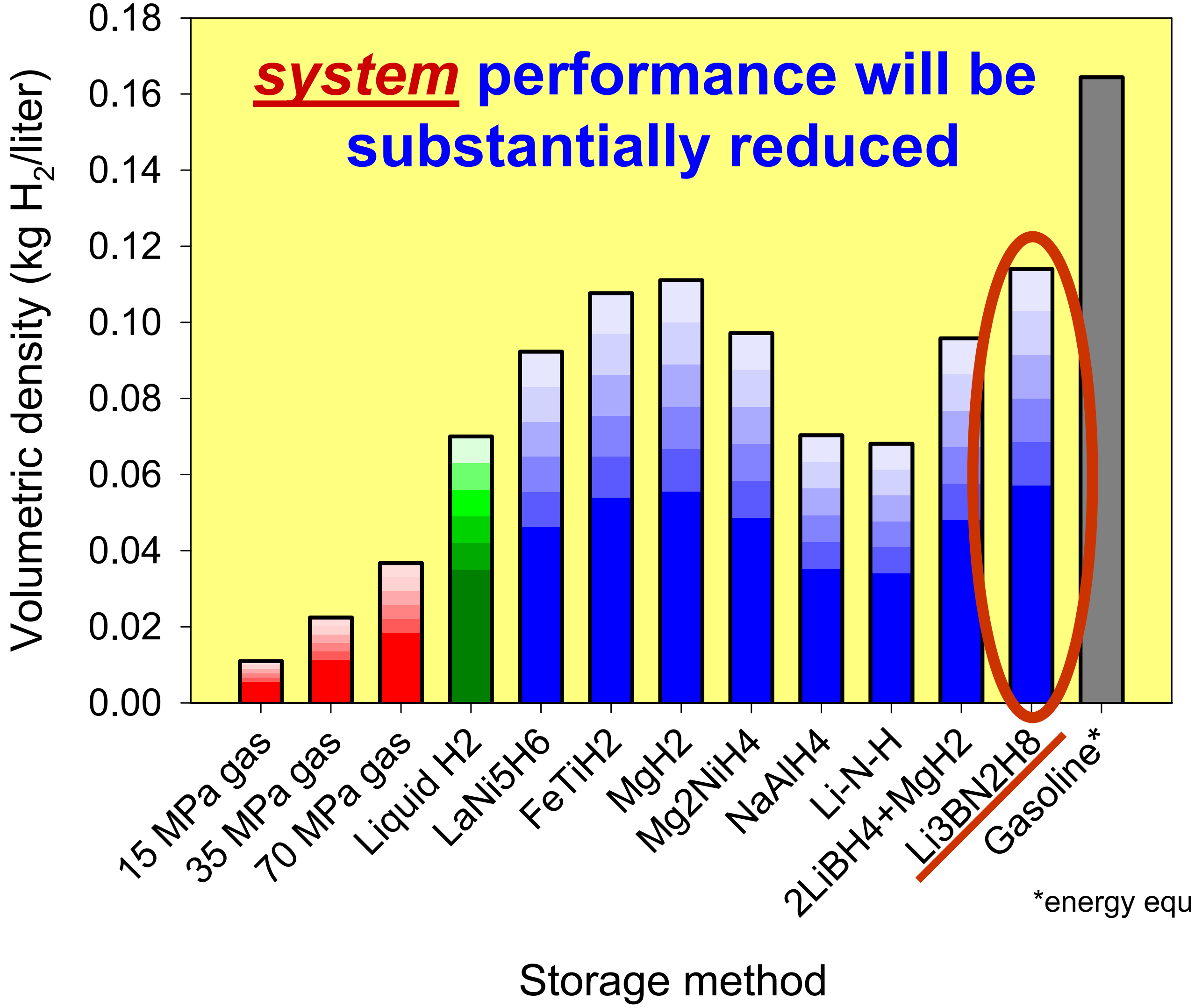
The hydrogen storage problem…

With thanks to Dr. Gert Arnold

Solid hydrides offer compact storage…

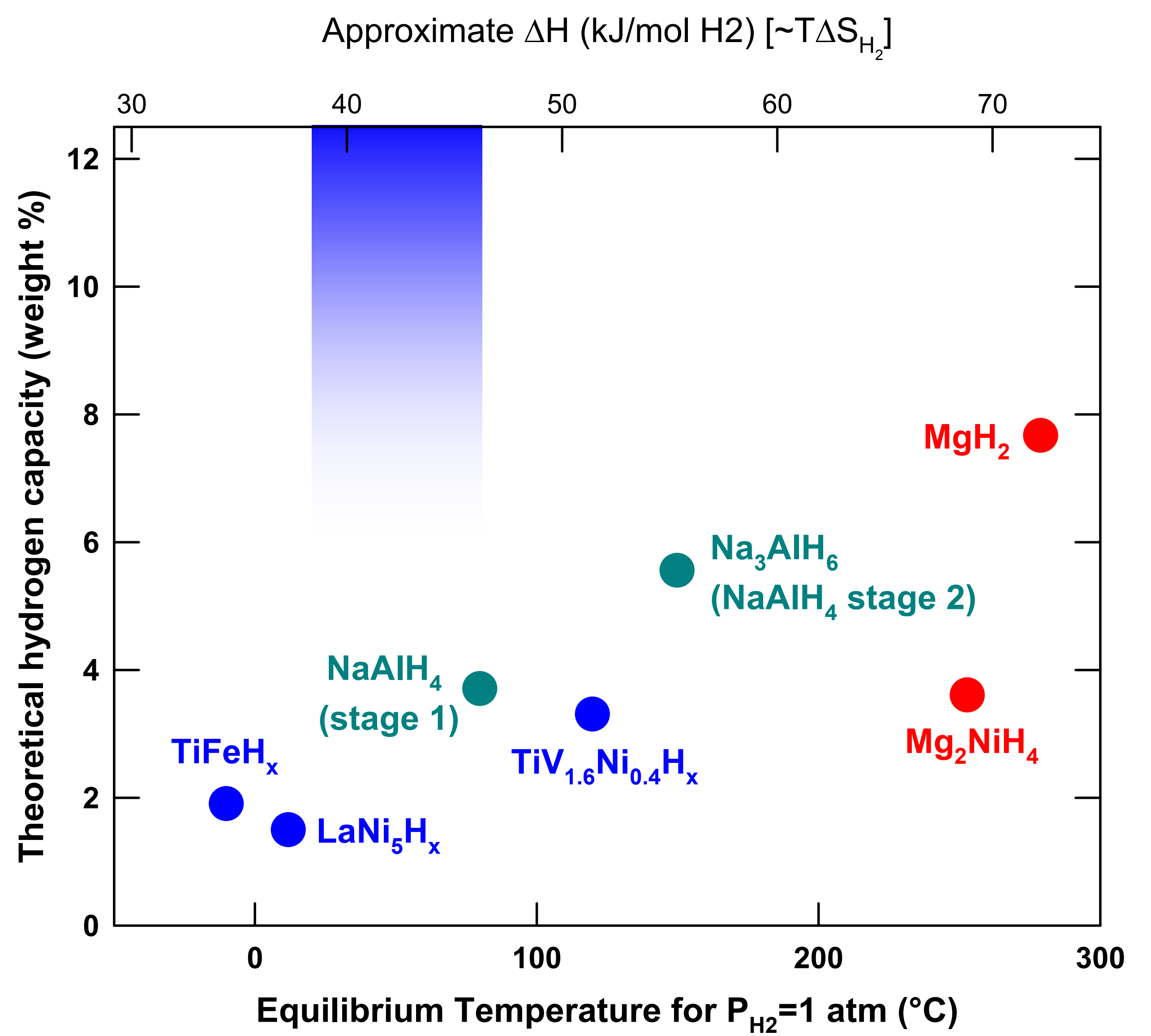


Solid hydrides offer compact storage…

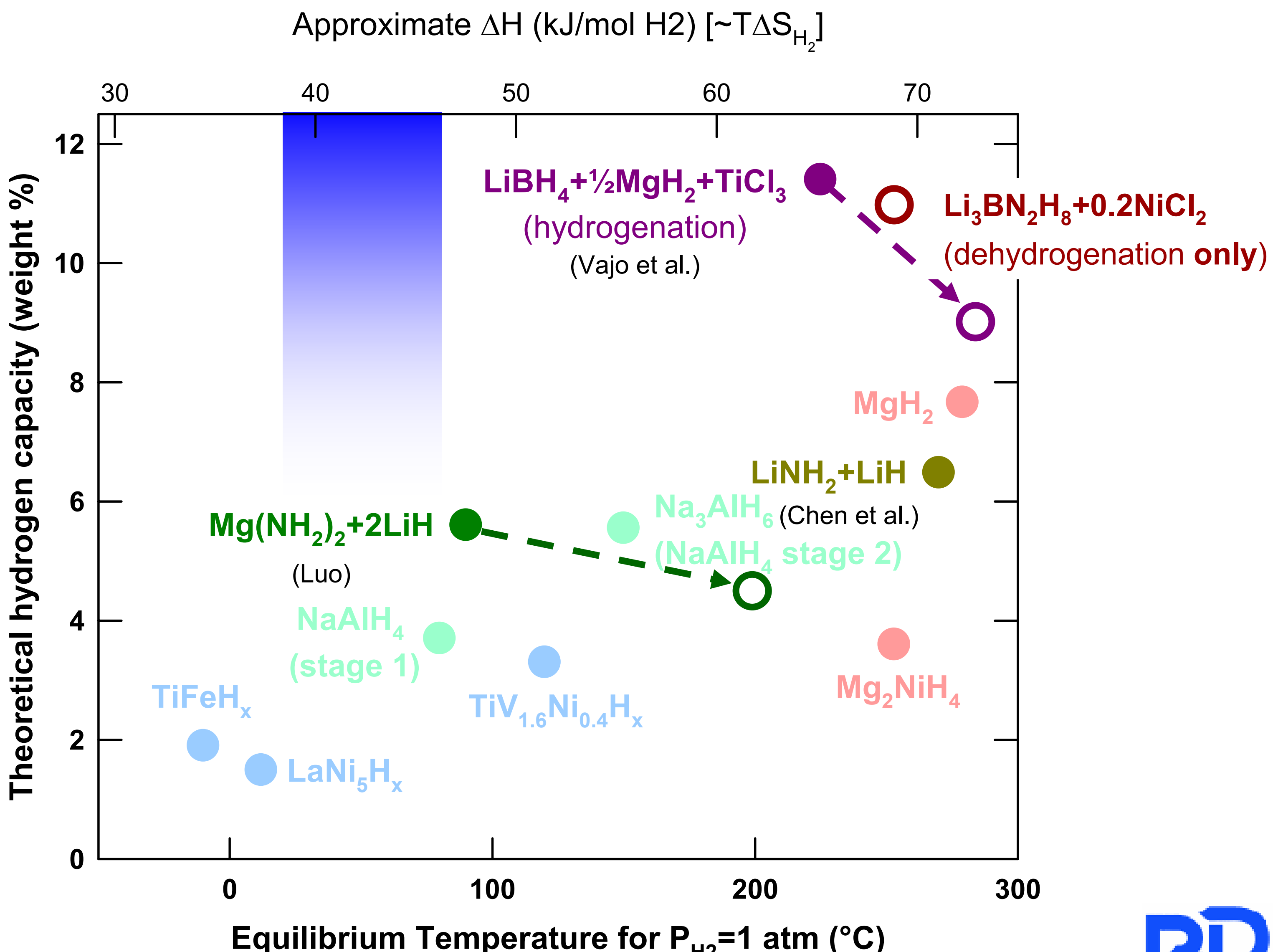


*energy equivalent

Other aspects are more challenging



Other aspects are more challenging



New materials research

- Capacity: High specific mass
- Thermodynamics: Moderate ΔH (~35 kJ/mol H_2)
  - Hydrogen release temperature 20-80 C in 2-5 bar H_2
  - Thermal management: insertion and extraction of ΔH
- Fast kinetics
  - Complex hydrides tend to be *kinetically* limited, requiring high temperature even if the thermodynamics are good

GM "Sequel" Hydrogen Fuel Cell prototype

Li-B-N-H: Building high-capacity reactions

$NaAlH_4 \rightarrow 1/3\ Na_3Al\mathbf{H}_6 + 2/3\ Al + H_2$	3.7 wt%	
$\rightarrow Na\mathbf{H} + Al + 3/2\ H_2$	5.6 wt%	(7.5 wt%)
$LiNH_2 + LiH \rightarrow Li_2N\mathbf{H} + H_2$	6.5 wt%	(9.8 wt%)
$Mg(NH_2)_2 + 2\ LiH \rightarrow Li_2Mg(N\mathbf{H})_2 + 2\ H_2$	5.6 wt%	(8.4 wt%)
$LiBH_4 \rightarrow Li\mathbf{H} + B + 3/2\ H_2$	13.9 wt%	(18.5 wt%)
$LiBH_4 + ½\ MgH_2 \rightarrow Li\mathbf{H} + ½\ MgB_2 + 2\ H_2$	11.5 wt%	(14.4 wt%)

Not all of the hydrogen is released

Strategy: Identify **HYDROGEN-FREE** compounds involving light elements that could be the **DECOMPOSITION PRODUCTS** of reactions between hydrogen-containing materials corresponding to **COMPLETE HYDROGEN RELEASE**

Hypothetical reaction

- Lithium Boronitride: Li_3BN_2
  - Several known polymorphs
    - Tetragonal $P4_22_12$ low temperature phase (<860°C)
      - a = 4.6435 Å c = 5.2592 Å
    - Monoclinic $P2_1/c$ high temperature phase
      - a = 5.1502 Å b = 7.0824 Å c = 6.7908 Å β = 112.96º
    - High pressure phase (DeVries and Fleischer)

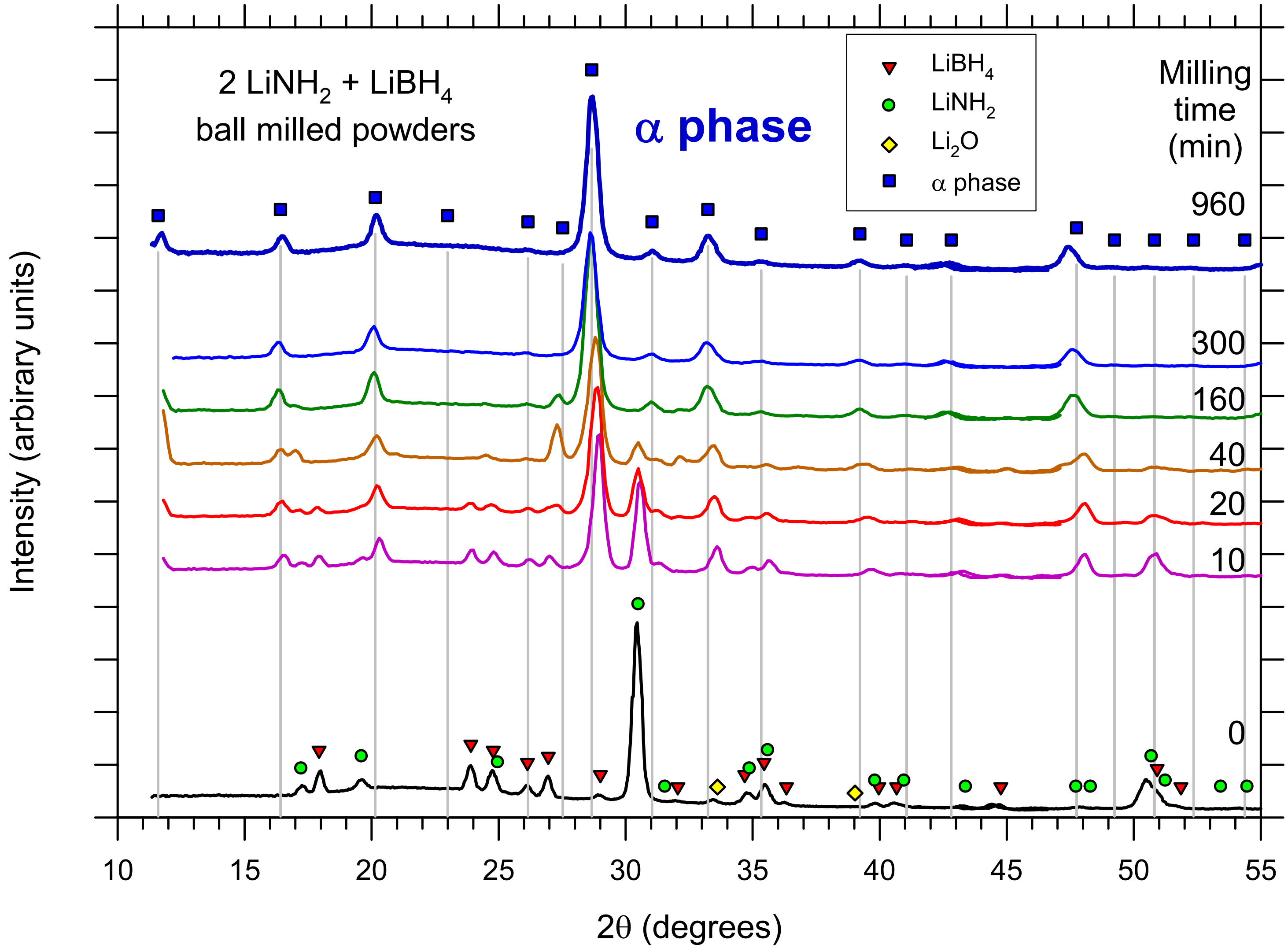
- Hypothetical reaction:

$$2\ LiNH_2 + LiBH_4 \rightarrow Li_3BN_2 + 4\ H_2 \quad 11.9\ wt\%\ H$$

- Success! > 11 wt% H_2 release
  - But here's the twist:

    We formed a new quaternary Li-B-N-H phase

Synthesis of 2 $LiNH_2$ + $LiBH_4$: Ball milling



Pinkerton et al., J. Phys. Chem. B 109, 6 (2005). Published on line: 17 Dec 2004

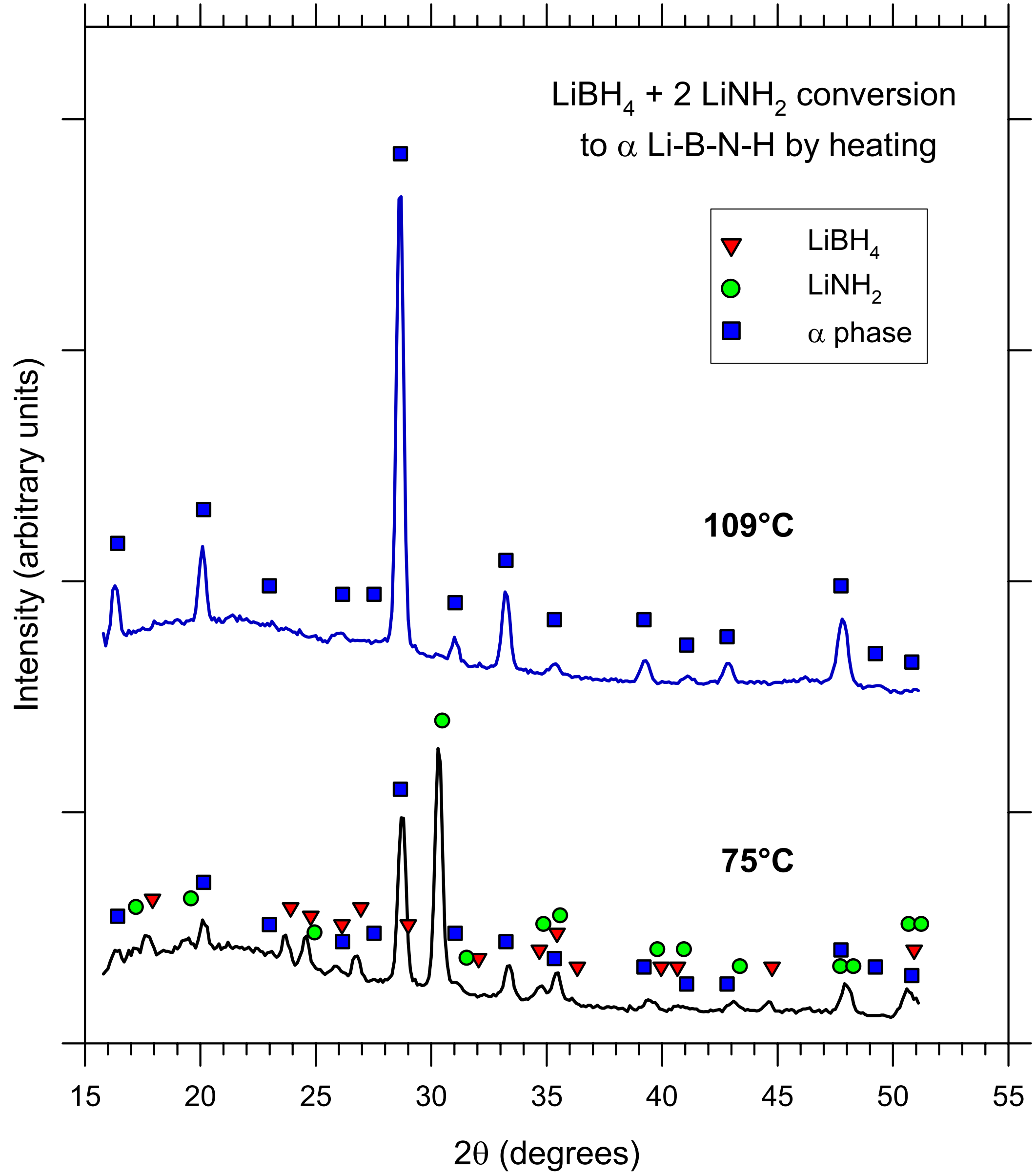
XRD Results:
Mix & Heat

Premill $LiNH_2$ and $LiBH_4$ separately for 10 min, then mix and heat

The *in situ* XRD data at 75ºC is identical to that at room temperature (RT) when the experiment started.

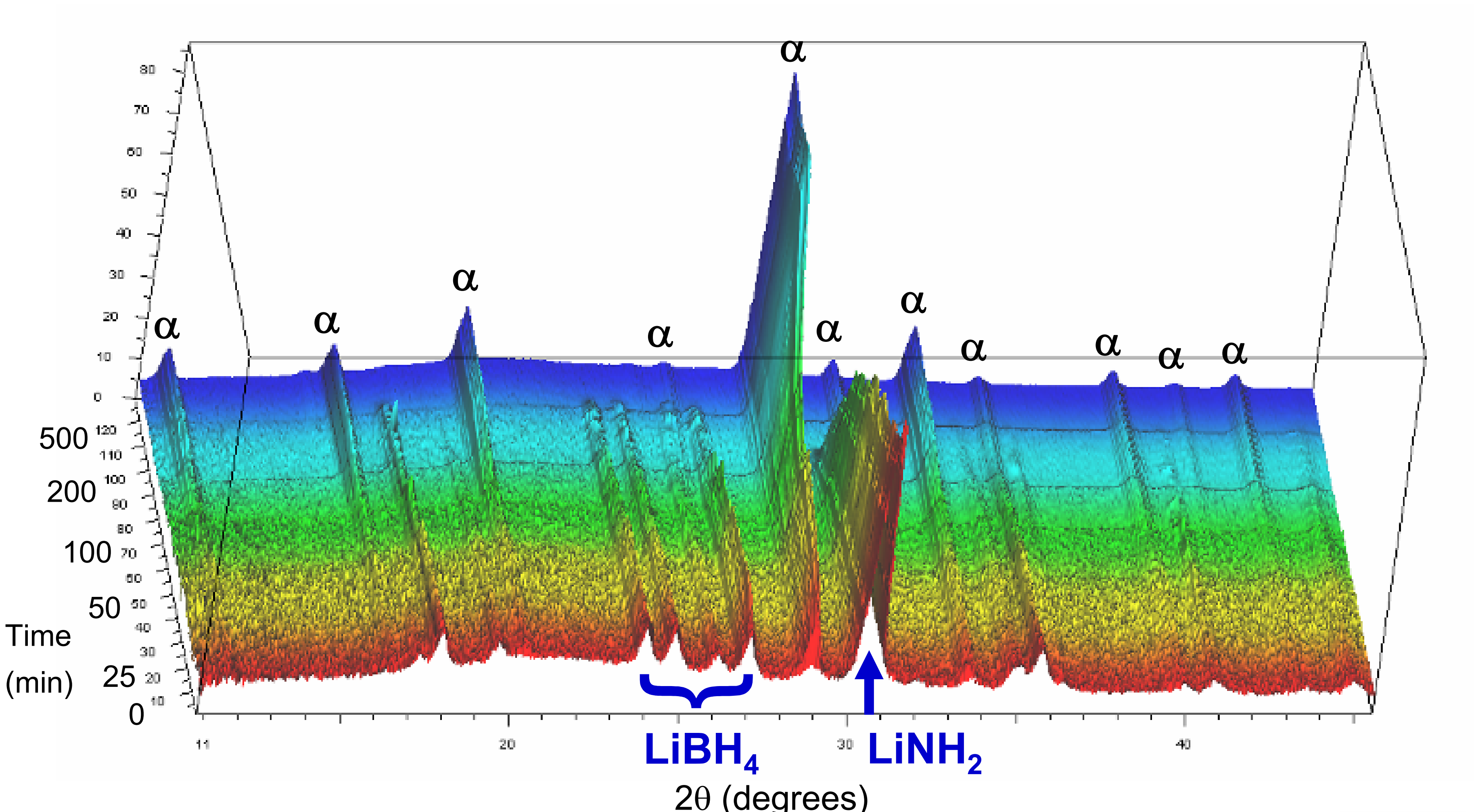
After mixing and storing for 12 days at RT, the mixture **spontaneously** formed a substantial quantity of the **α phase**!

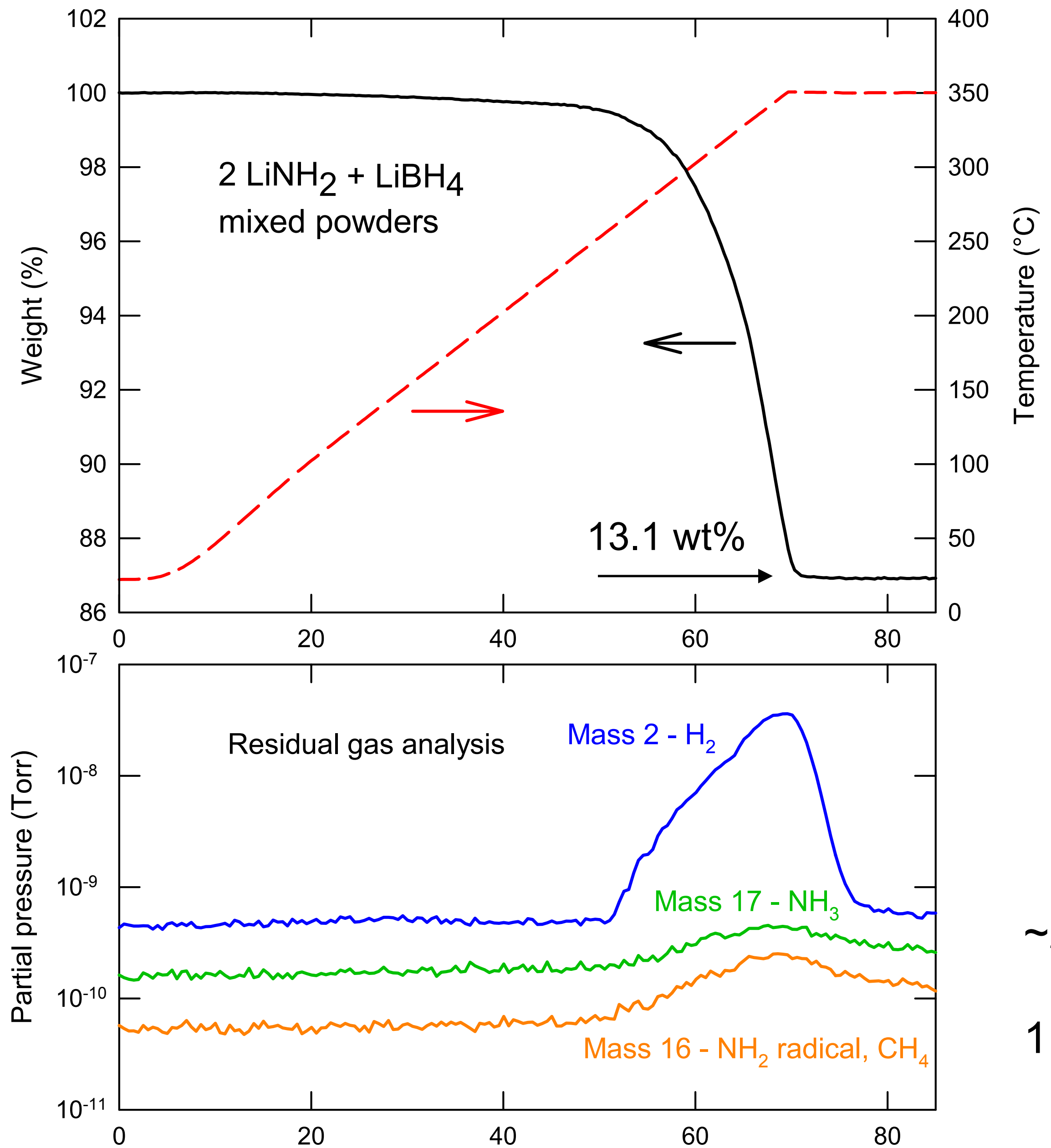
Heating above ~95ºC completes the conversion to the **α phase**.



Pinkerton et al., J. Phys. Chem. B 109, 6 (2005).

In situ XRD: Evolution of α Li-B-N-H at 73 °C





Hydrogen desorption (TGA)

2 $LiNH_2$ + $LiBH_4$
mixed powders
(“mix and heat”)

13.1 wt% loss
exceeds theoretical
H_2 content (11.9%)

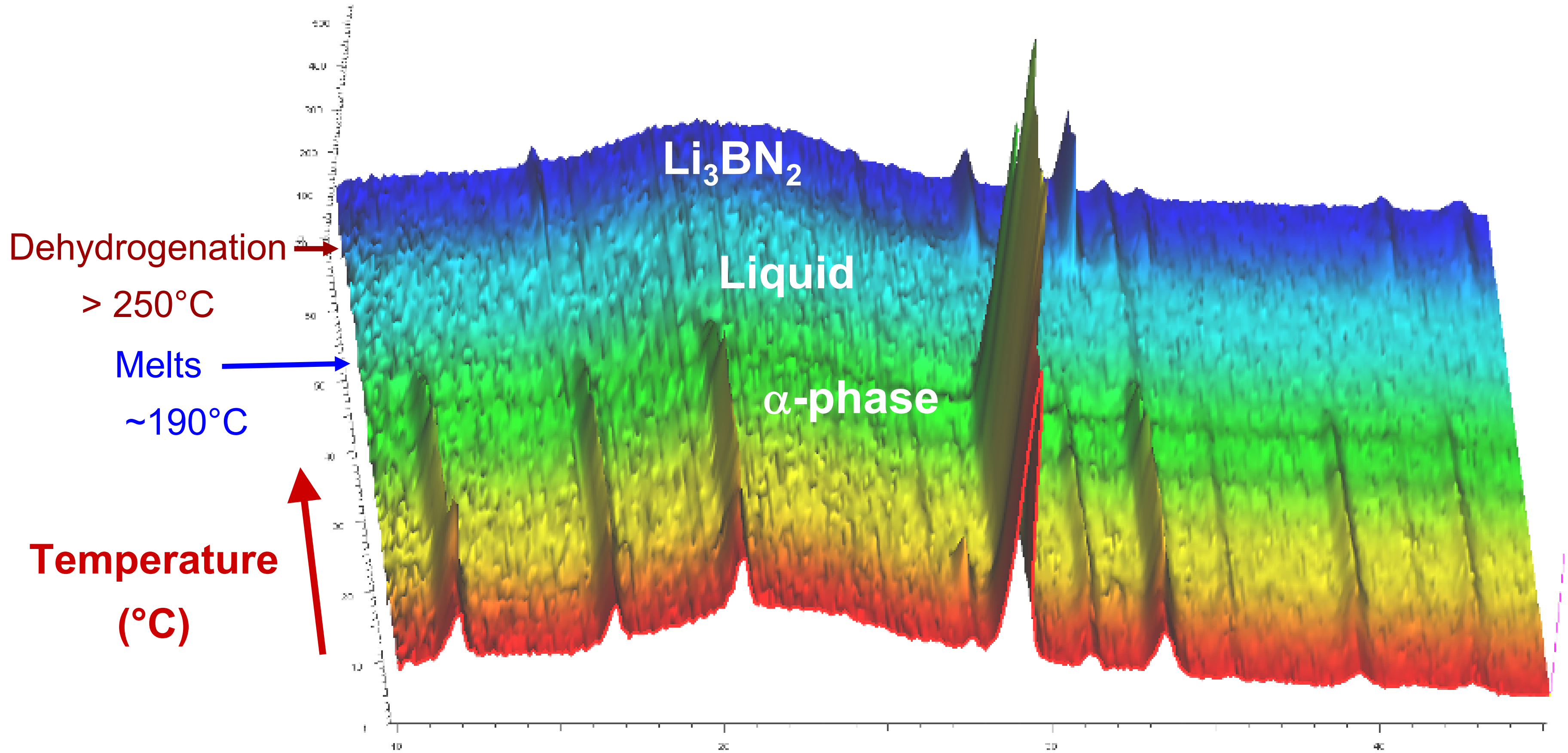
RGA mass spectrometry

~2 mole% NH_3

11.5 wt% H_2, 1.6 wt% NH_3

Pinkerton et al., J. Phys. Chem. B 109, 6 (2005).

In situ XRD – ball milled $2LiNH_2 + LiBH_4$



Reaction path

$2\ LiNH_2 + LiBH_4 \rightarrow \alpha$ Li-B-N-H (solid)

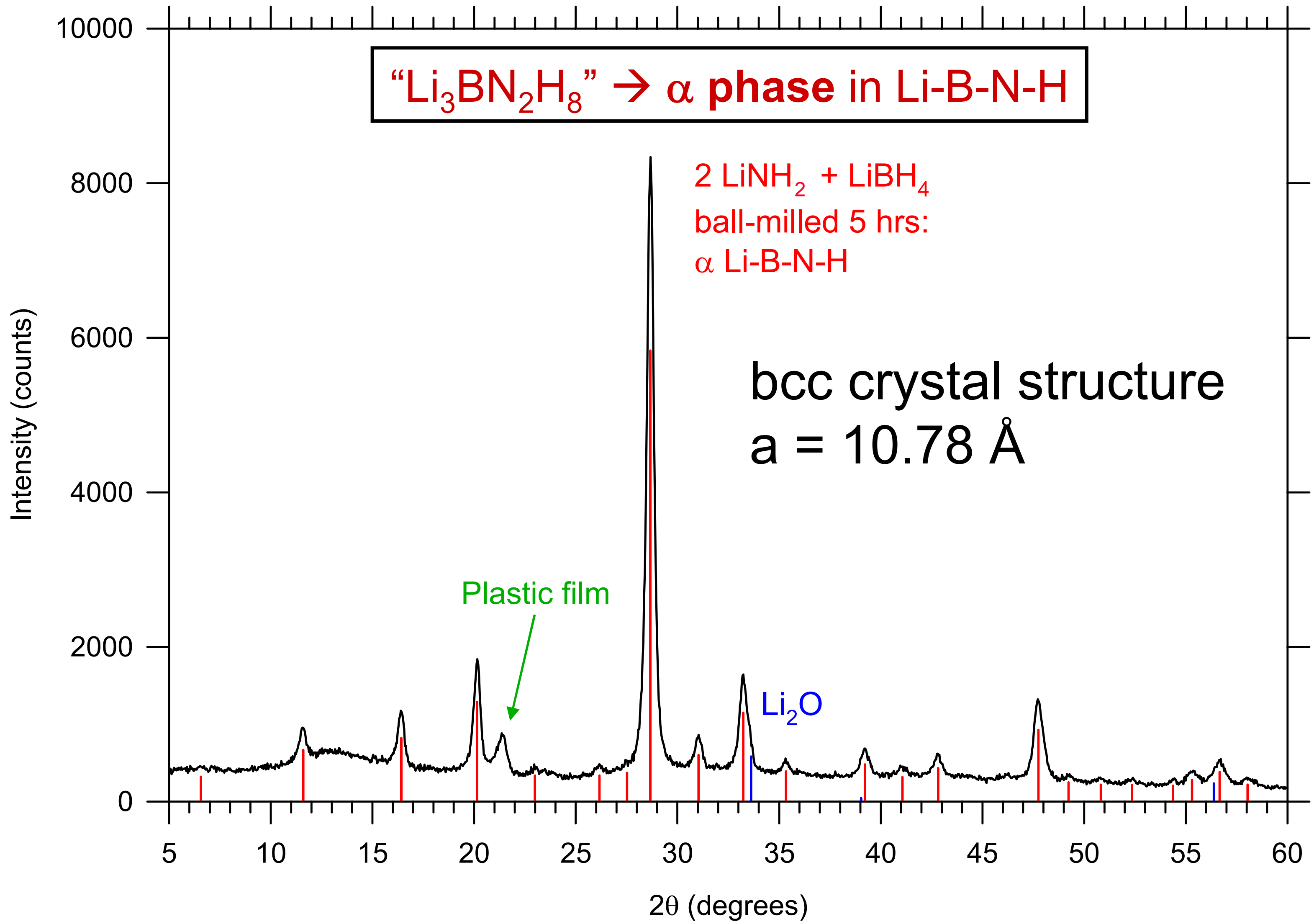
$\rightarrow \alpha$ Li-B-N-H (liquid) ~195ºC

$\rightarrow Li_3BN_2$ (solid) + $4\ H_2$ >250ºC

"Destabilized $LiBH_4$" ?

New compound, less stable than $LiBH_4$

α *Li-B-N-H:* a new quaternary hydride



α-phase crystal structure

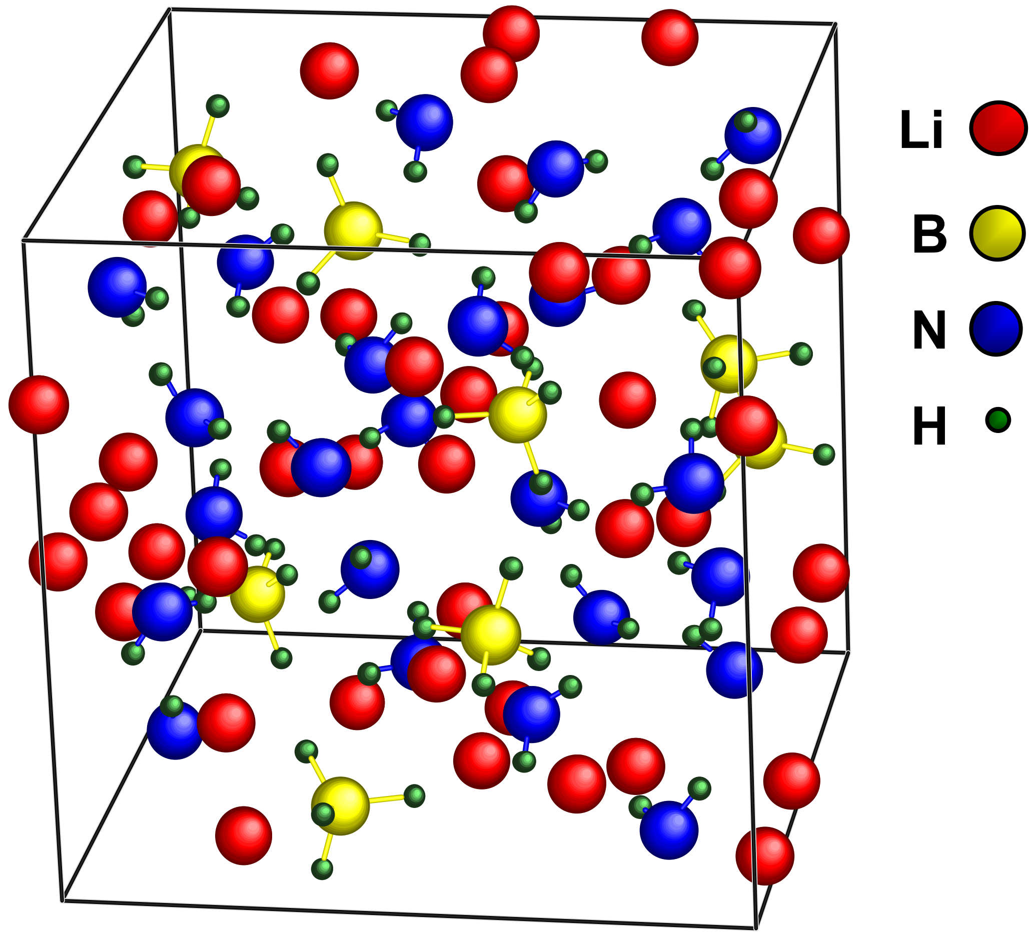
- Single crystals formed by recrystallizing from the melt
- Body-centered cubic space group:

  $I2_13$ (#199)

  a = 10.676 Å
- NH_2^- and nearly tetrahedral BH_4^- units persist in the structure
- Equilibrium composition:

  $Li_4BN_3H_{10}$!

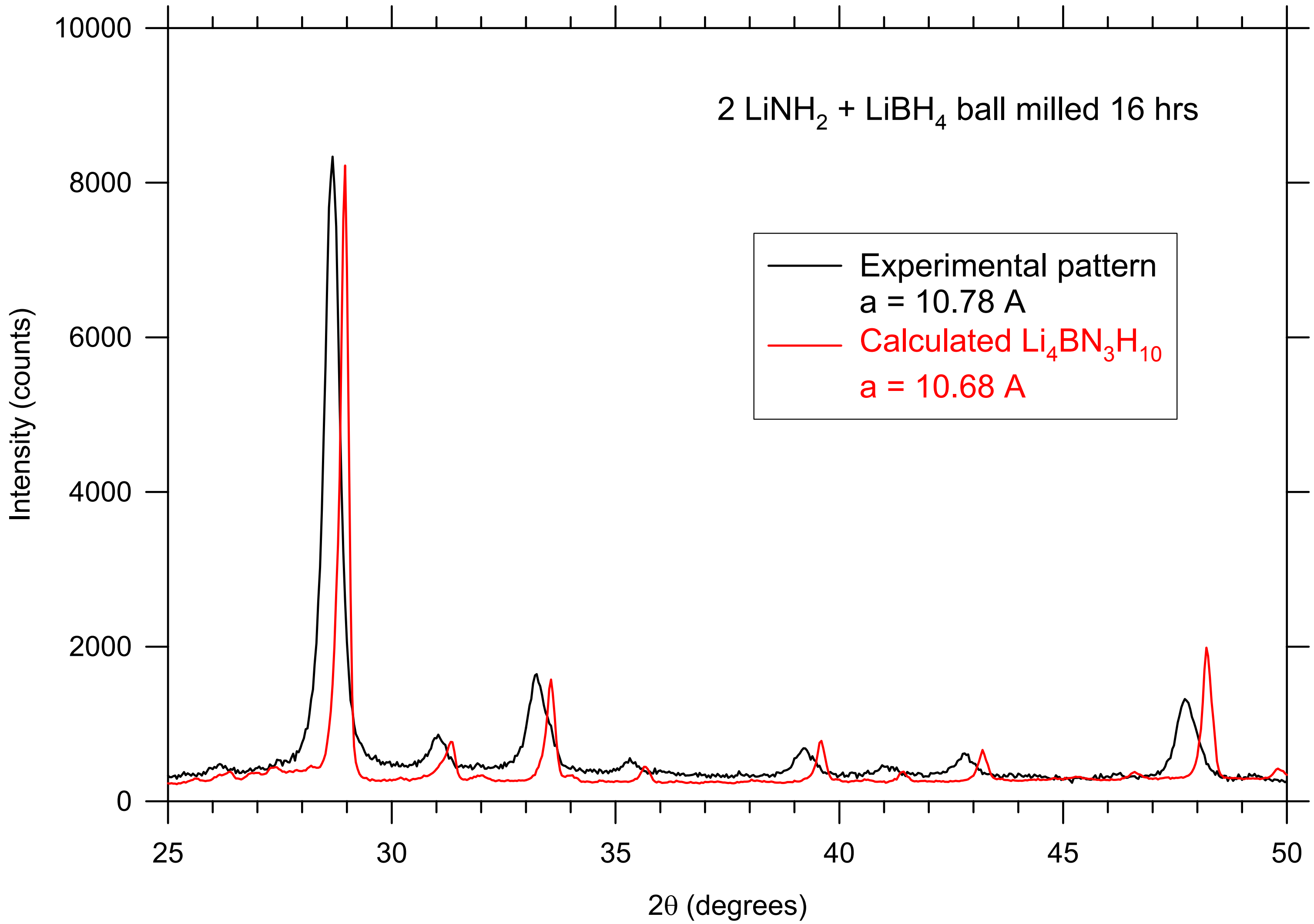
  (= **3** $LiNH_2$ + $LiBH_4$)



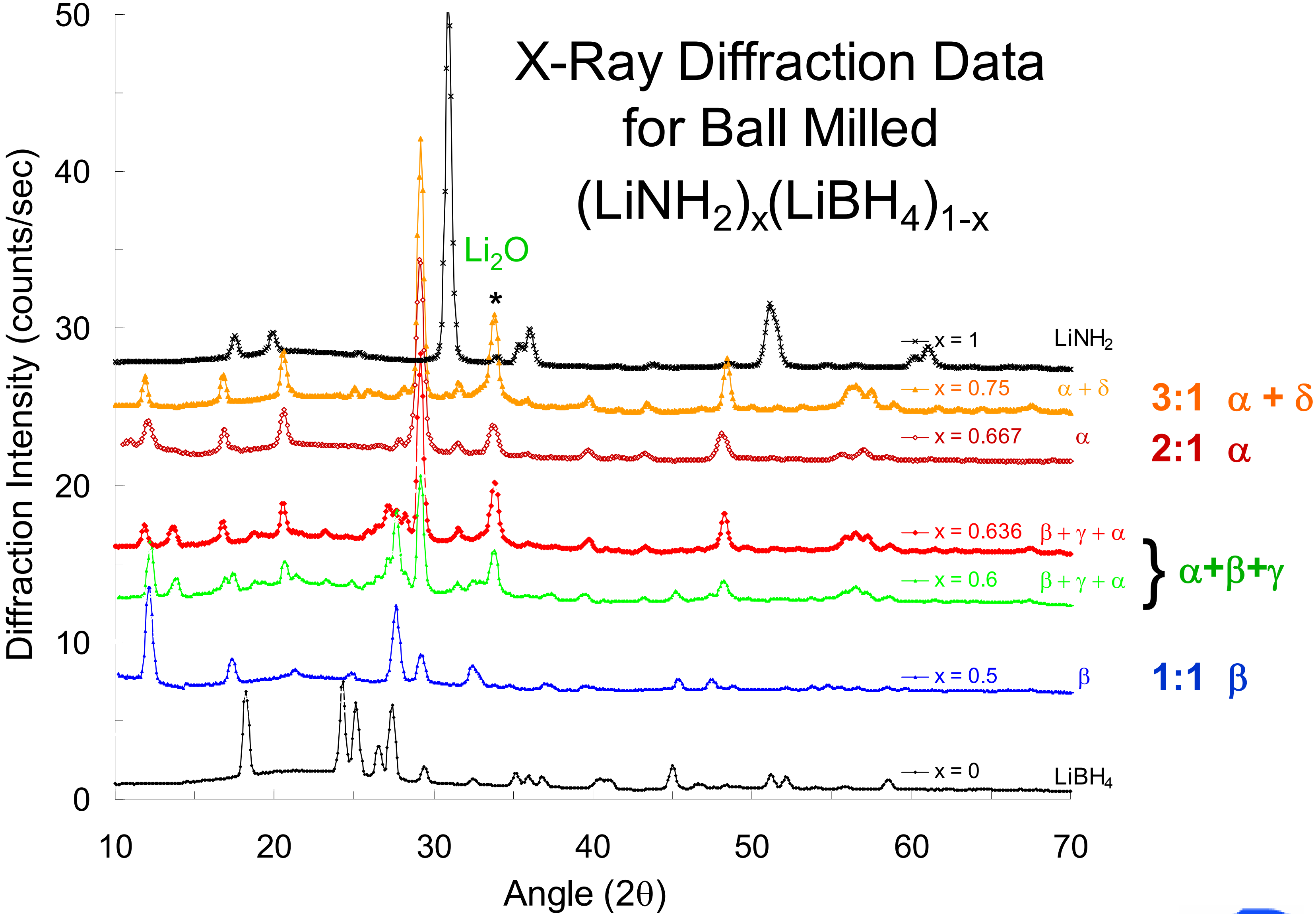
Filinchuk et al., Inorg. Chem. 45, 1433 (2006).

Université de Genève

Lattice shift of ball milled material



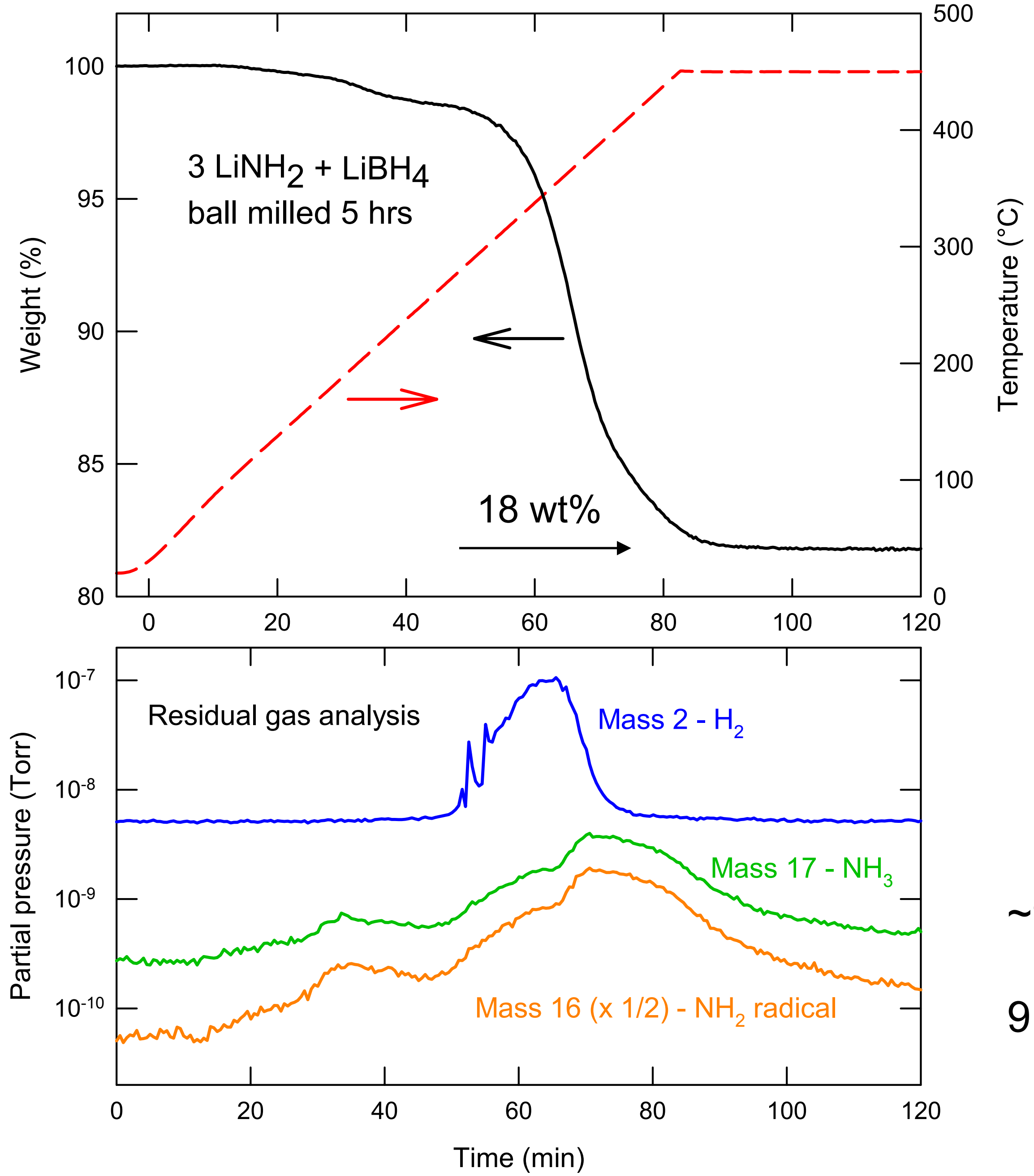
X-Ray Diffraction Data for Ball Milled $(LiNH_2)_x(LiBH_4)_{1-x}$



Meisner et al., J. Phys. Chem. B 110, 4186 (2006).

What about <u>3</u> $LiNH_2 + LiBH_4$?

If the α phase is $Li_4BN_3H_{10}$, then what is the dehydrogenation behavior of samples made at the 3 $LiNH_2 + LiBH_4$ composition?



Hydrogen desorption (TGA)

$3\ LiNH_2 + LiBH_4$

Ball milled 5 hrs

18 wt% loss

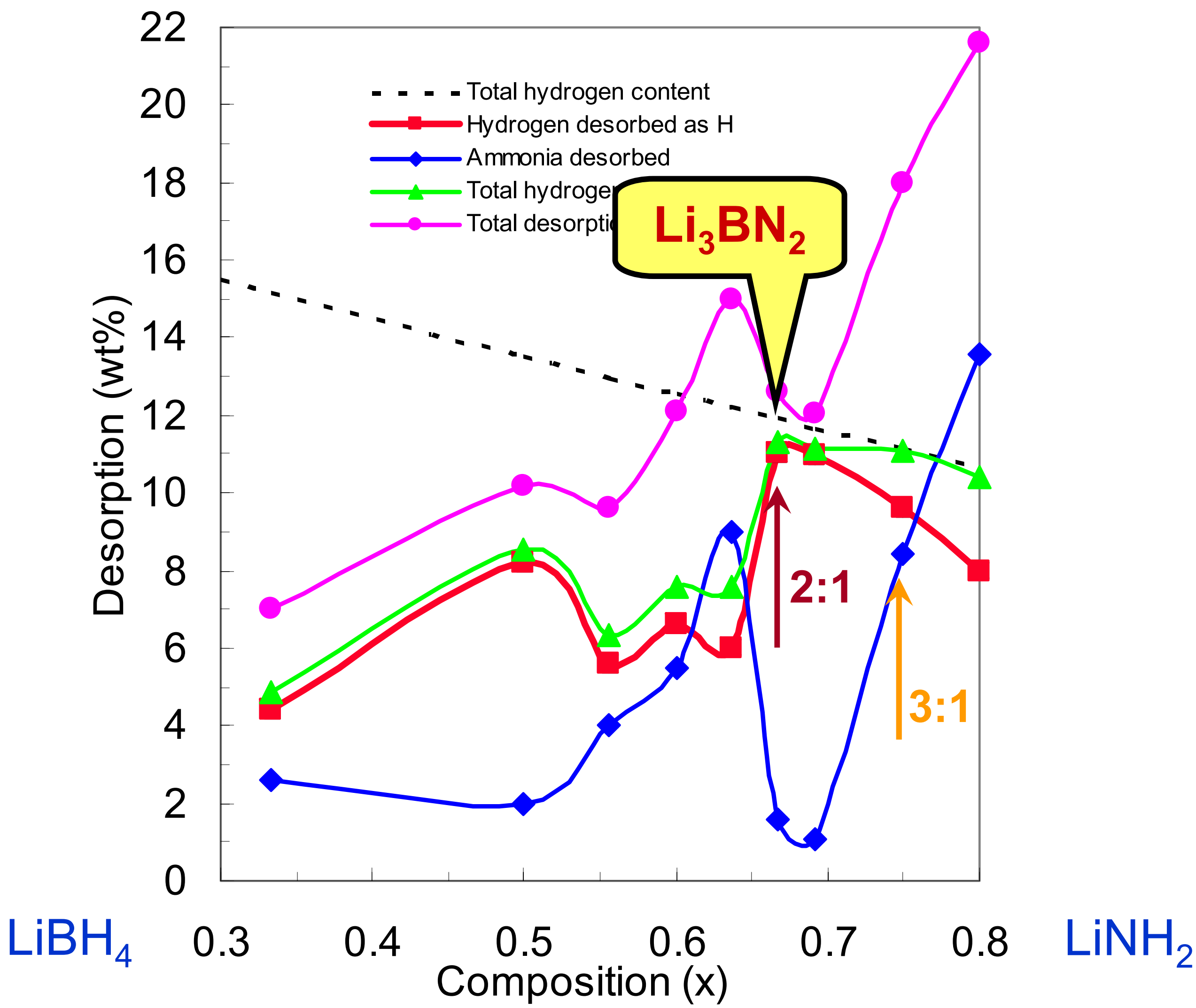
(theoretical content 11.1 wt%)

RGA mass spectrometry

~9 mole% NH_3

9.6 wt% H_2, 8.3 wt% NH_3

H_2 and NH_3 release in $(LiNH_2)_x(LiBH_4)_{1-x}$



Meisner et al., J. Phys. Chem. B 110, 4186 (2006).

GM

What's so special about 2:1?

Li_3BN_2 !

- Dehydrogenation from the liquid is not controlled by the starting α-phase, but rather by the product Li_3BN_2 phase

- For 2 $LiNH_2$ + $LiBH_4$:

  $Li_3BN_2H_8$ (liquid) → Li_3BN_2 + $4H_2$

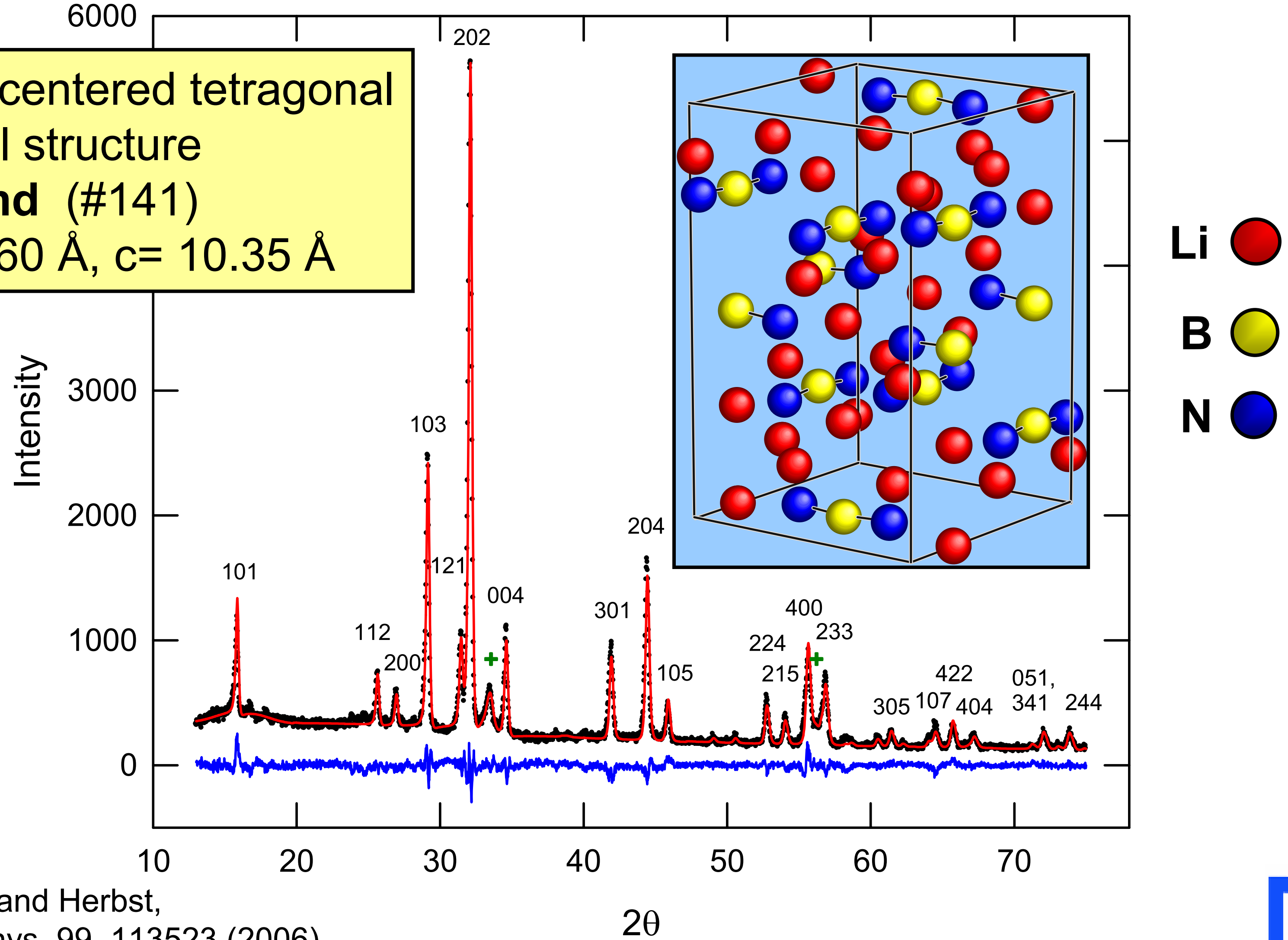
- For 3 $LiNH_2$ + $LiBH_4$:

  $Li_4BN_3H_{10}$ (liquid) → Li_3BN_2 + ½ Li_2NH + $4H_2$ + ½ NH_3

R&D CENTER

Dehydrogenated material: New Li_3BN_2 polymorph

Body-centered tetragonal crystal structure
$I4_1$/amd (#141)
a = 6.60 Å, c= 10.35 Å



Pinkerton and Herbst,
J. Appl. Phys. 99, 113523 (2006).

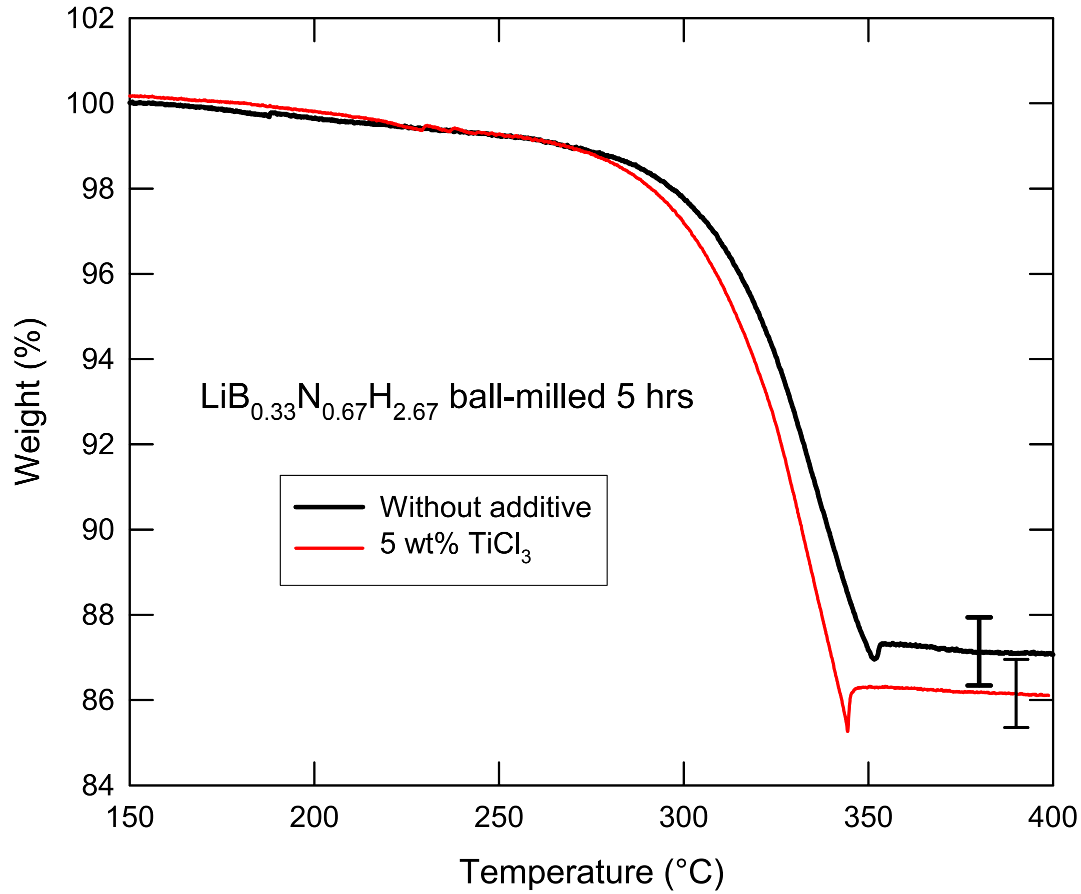
Promoting H_2 release with metal additives

- Composition: $2\ LiNH_2 + LiBH_4$ + additive
- All samples ball milled for 5 hrs
  - Fully converted to α **phase**
- Metals or metal compounds added prior to ball milling
  - Metal powder
  - Metal dichlorides
  - “Pt/Vulcan carbon”: 2 nm diameter Pt nanoparticles supported on a Vulcan carbon substrate

$TiCl_3$ additive

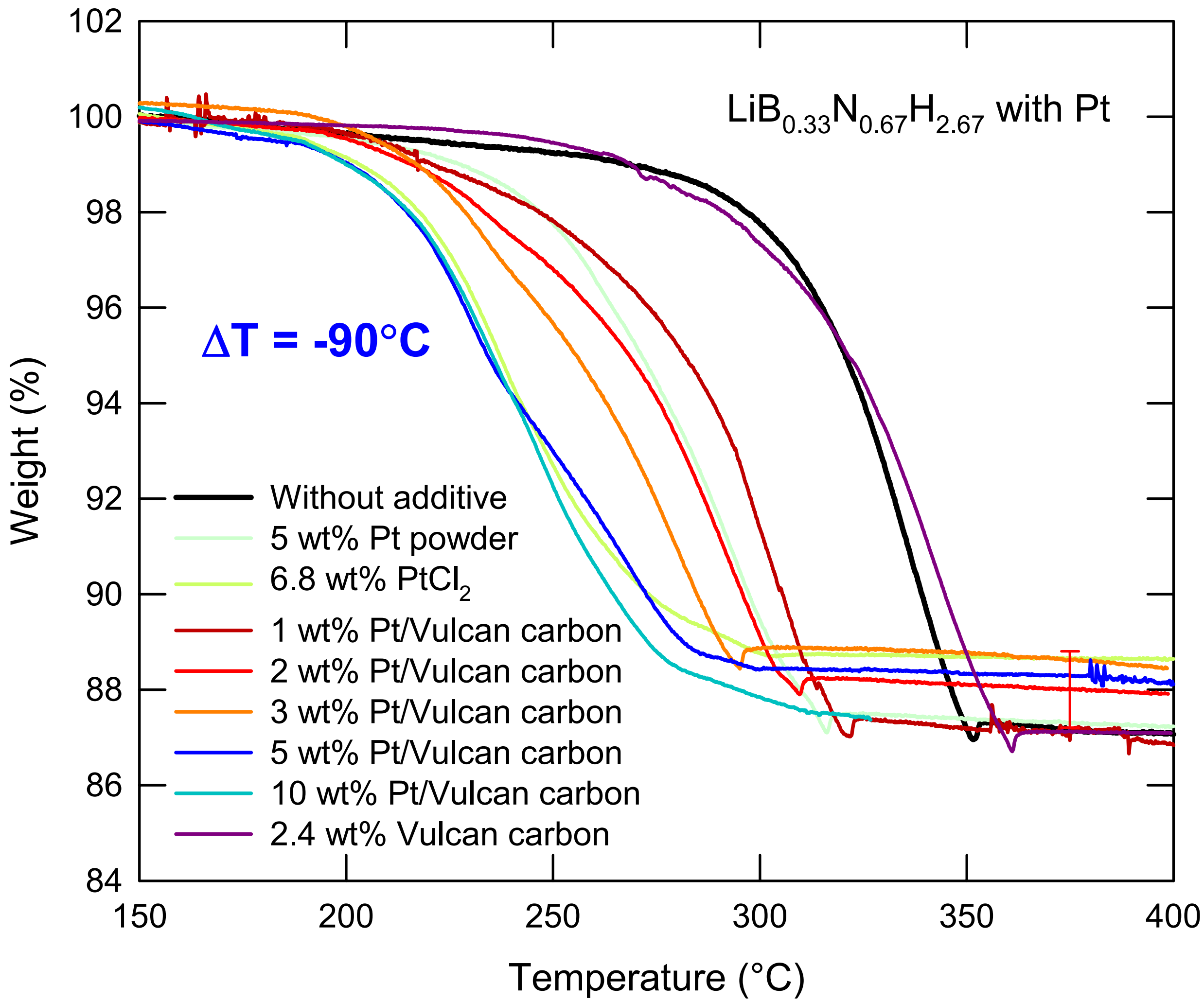
- 2 mole% $TiCl_3$ additive has been shown to be very effective in some hydrogen storage systems
  - $NaAlH_4$ (Bogdanović et al.)
  - $LiBH_4$ + ½ MgH_2 (Vajo et al.)

- **$TiCl_3$ does not significantly improve dehydrogenation of Li-B-N-H**



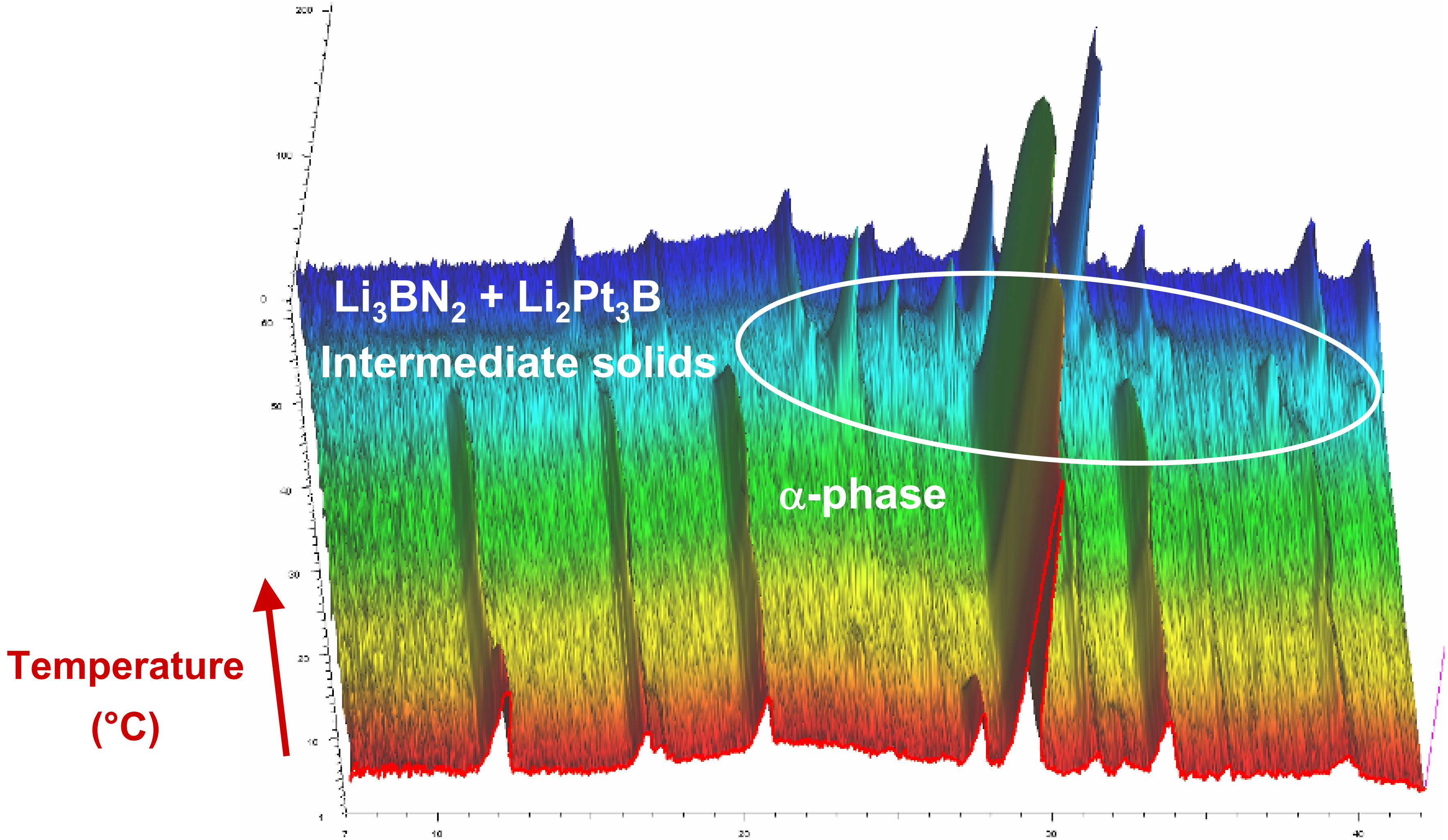
Pinkerton et al., J. Phys. Chem. B 110, 7967 (2006).

Pt/Vulcan carbon additions



Pinkerton et al., J. Phys. Chem. B 110, 7967 (2006).

In situ XRD – Pt/Vulcan carbon added



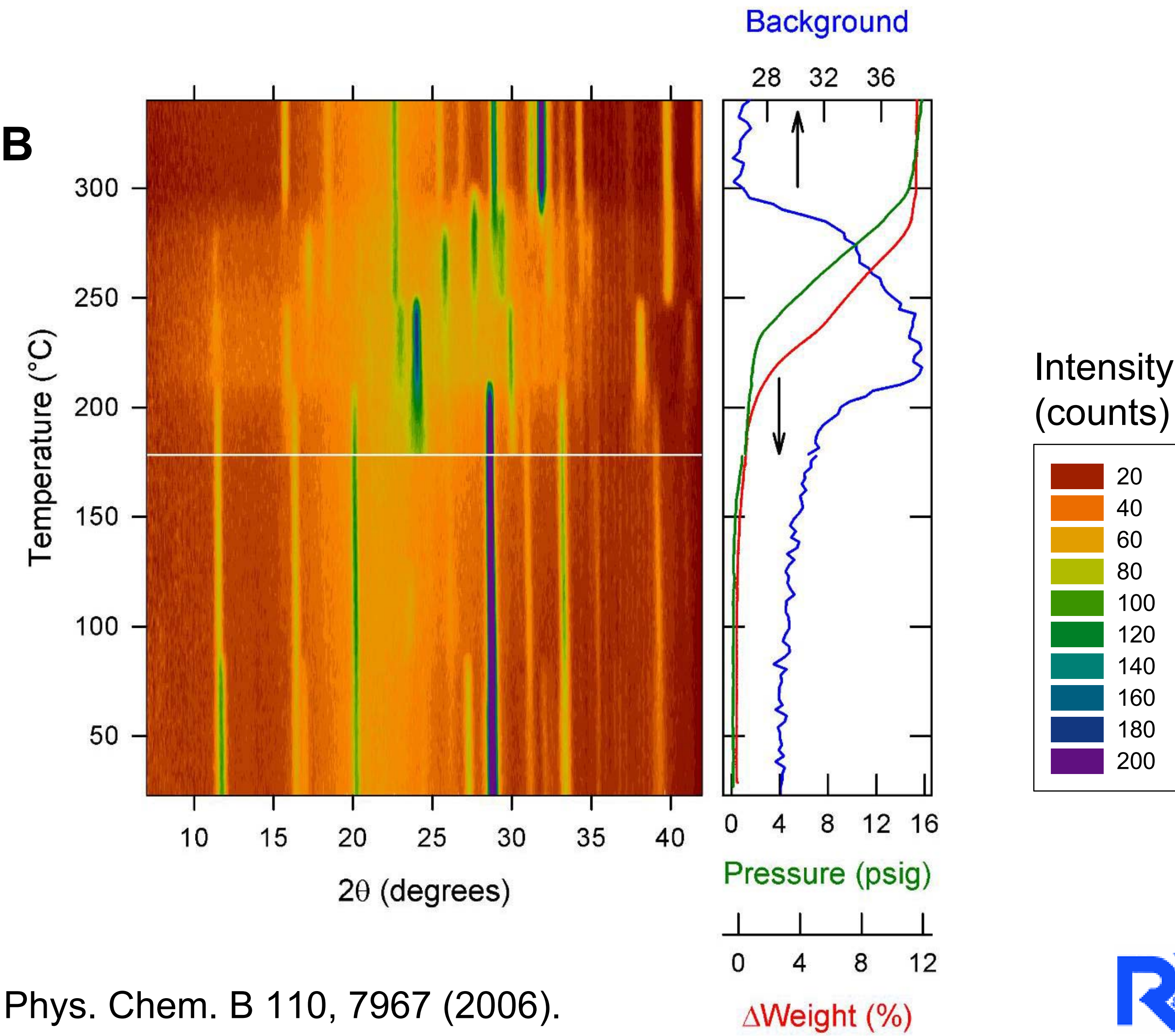
In situ XRD - 5 wt% Pt/Vulcan carbon

$Li_3BN_2 + Li_2Pt_3B$

Intermediate 2

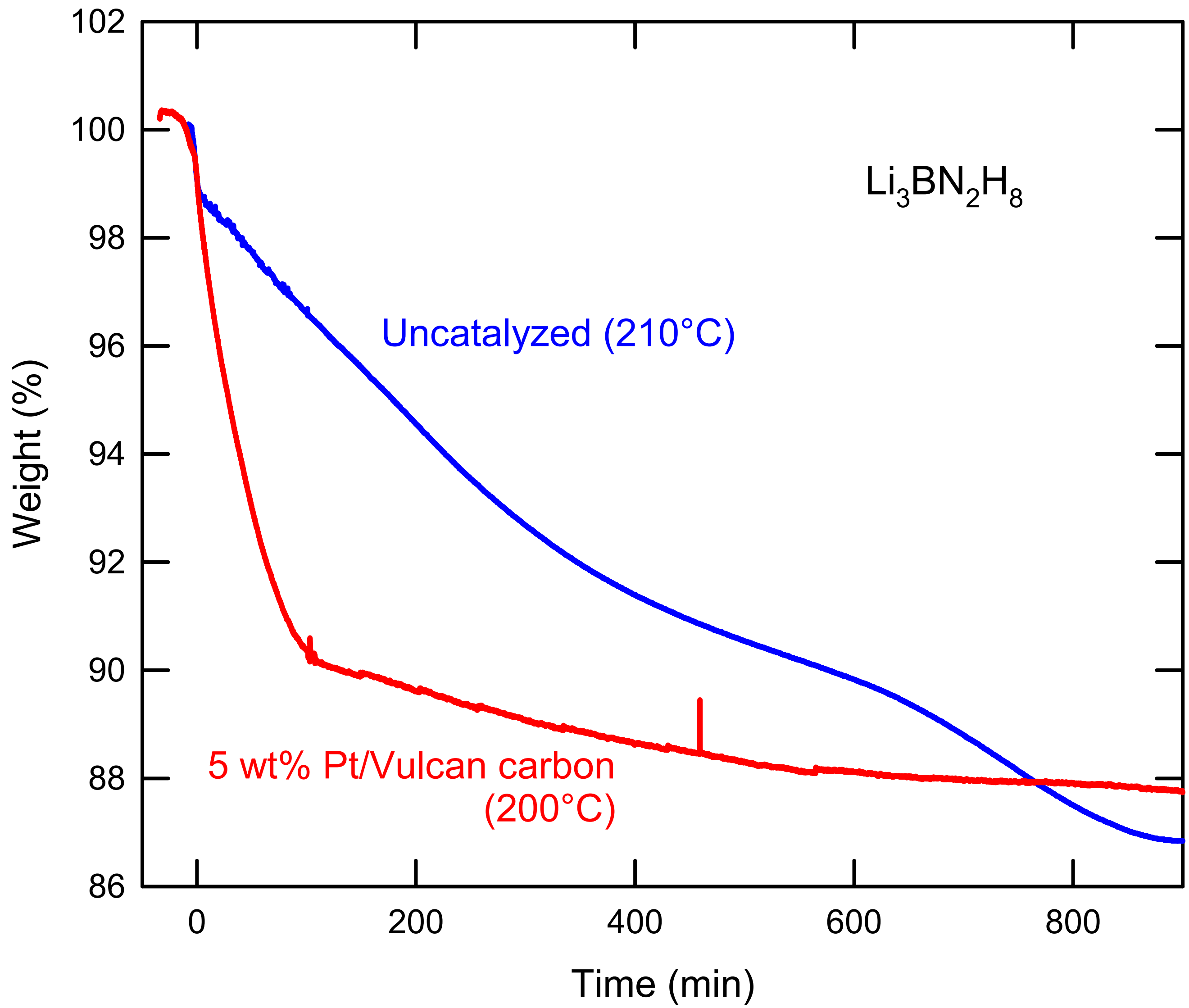
Intermediate 1

Quaternary
α-phase

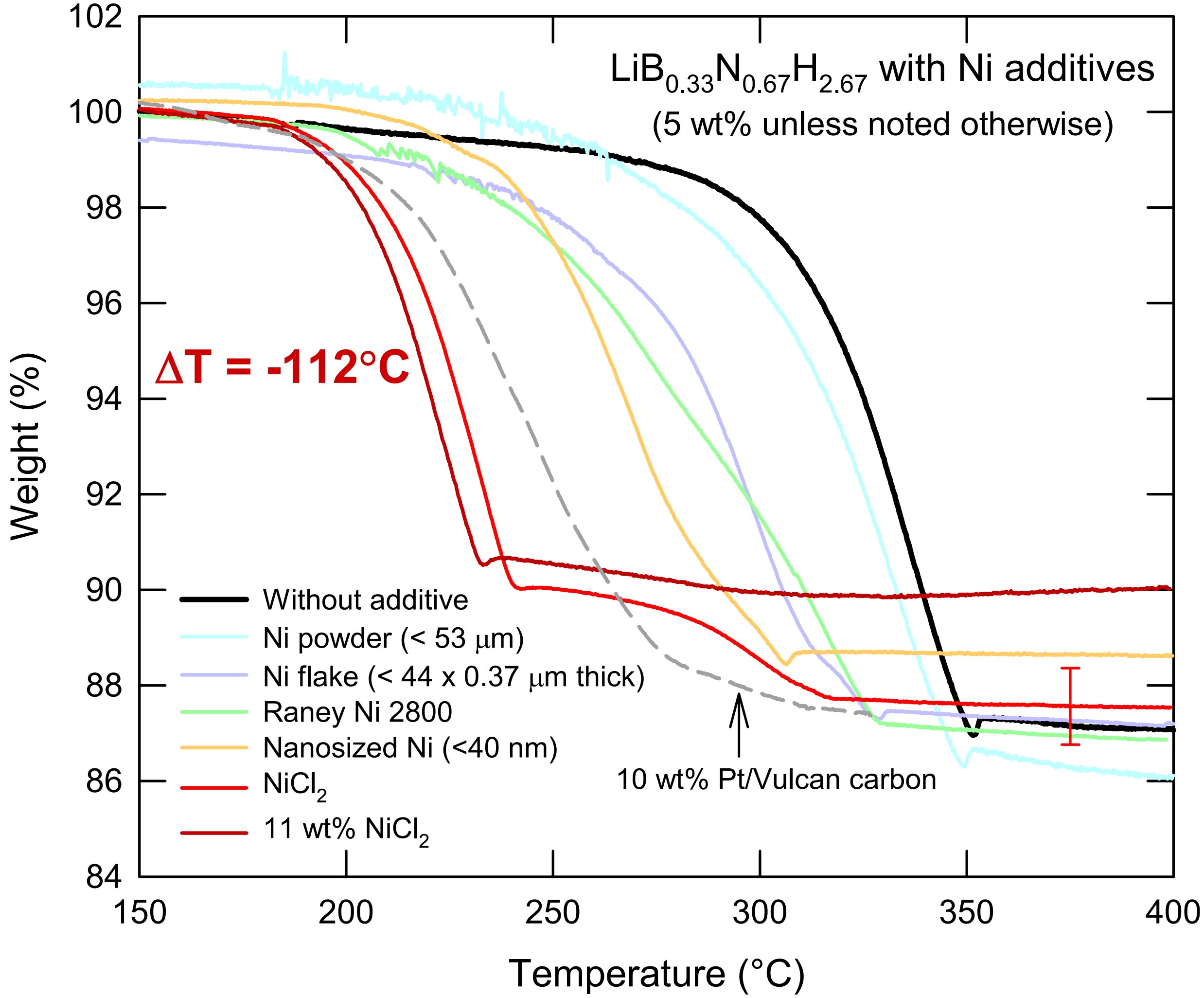


Pinkerton et al., J. Phys. Chem. B 110, 7967 (2006).

Accelerated isothermal H_2 release

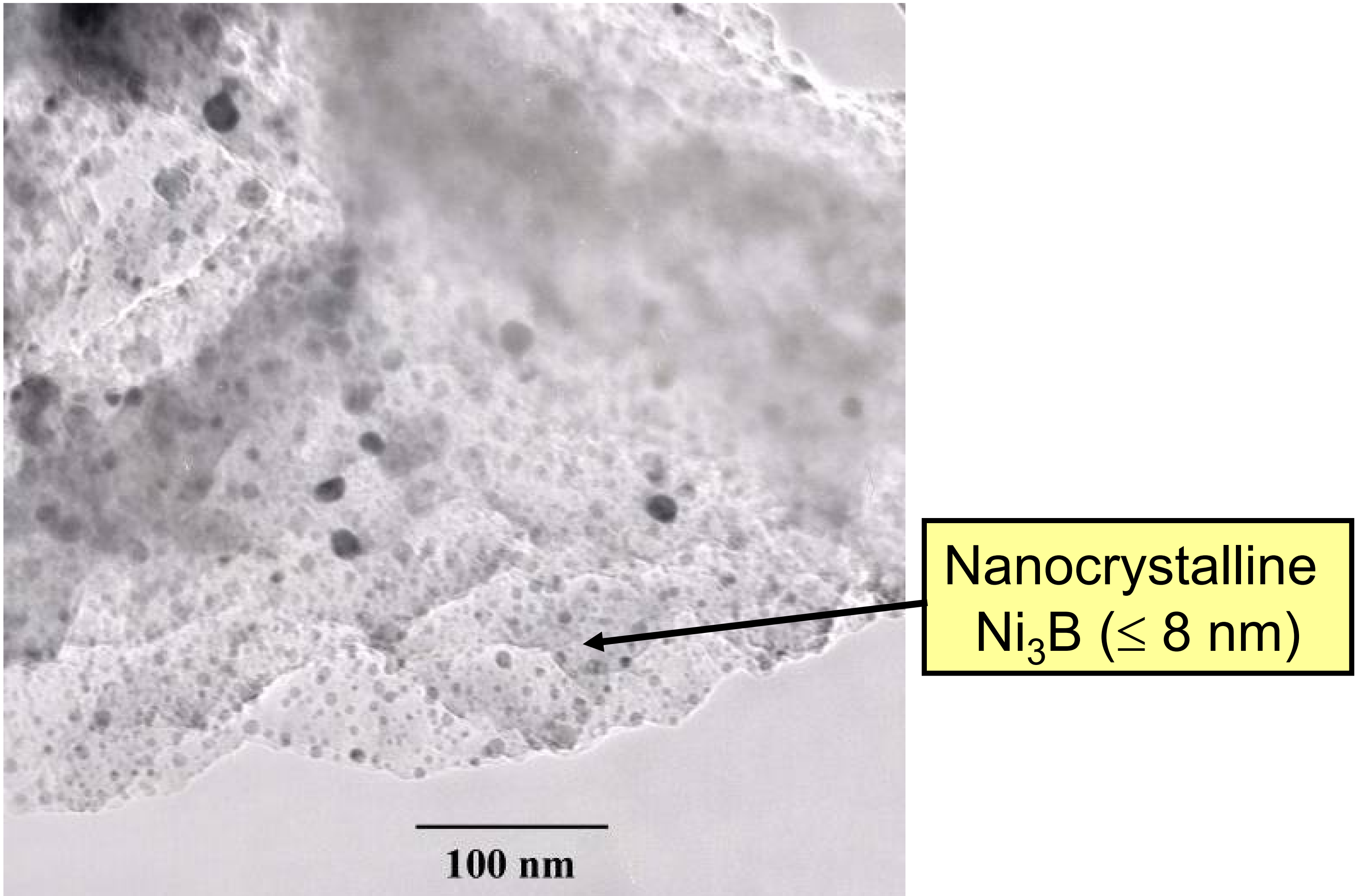


$NiCl_2$ additions



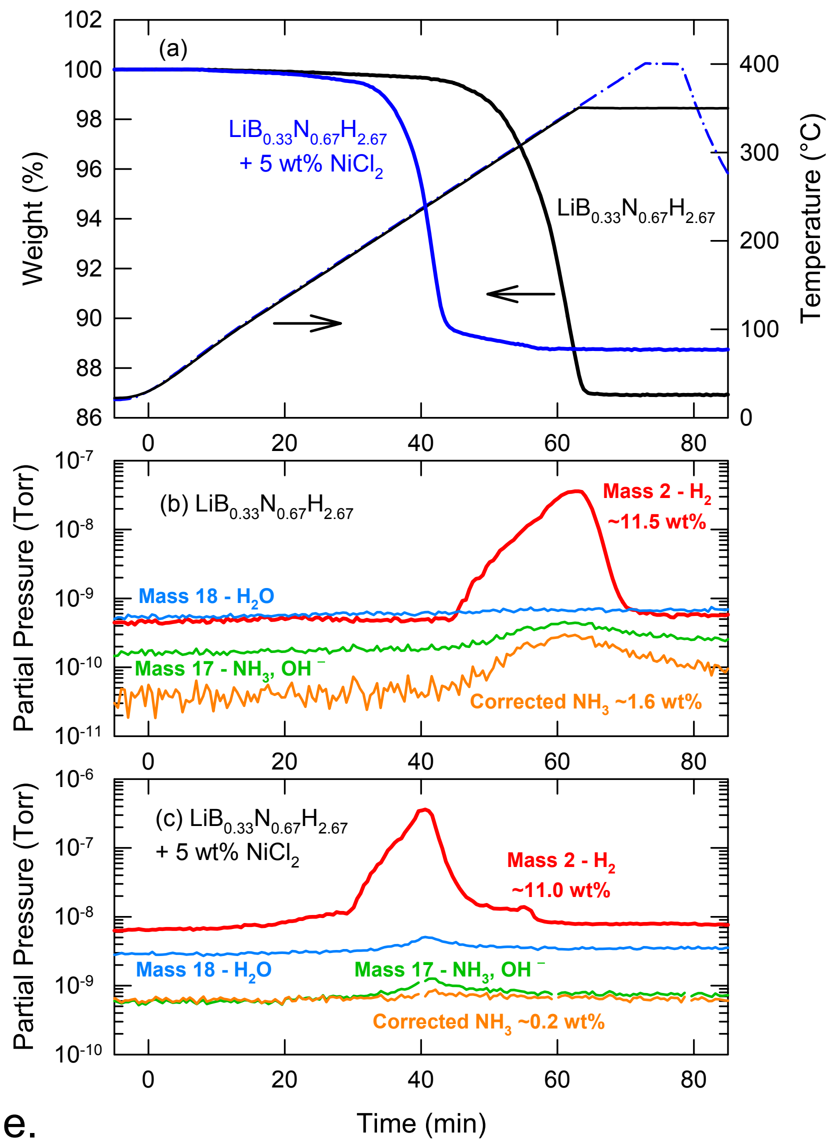
Pinkerton et al., JALCOM, available online.

TEM: $LiB_{0.33}N_{0.67}H_{2.67}$ + 5 wt% $NiCl_2$



Mass spectrometry gas analysis

- Additive-free Li-B-N-H:
  - H_2 and NH_3 release occur together above 250°C
  - Evolved gas ~2 mole% NH_3
- $NiCl_2$-added:
  - onset of H_2 release is 120°C
  - Total NH_3 release reduced by an order of magnitude



Pinkerton et al., JALCOM, available online.

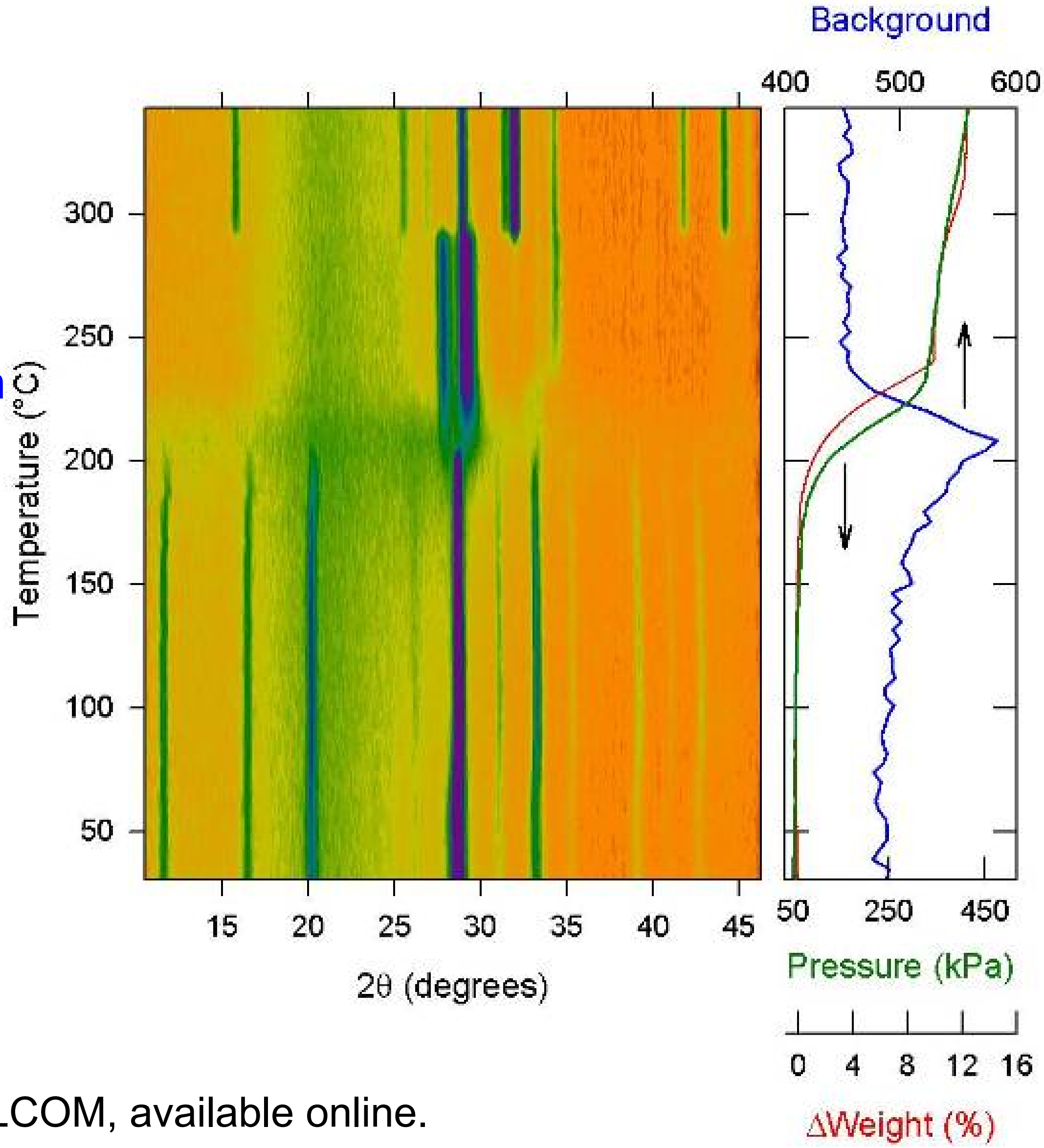
5 wt% $NiCl_2$ addition

Li_3BN_2

Intermediate

Distinct from both intermediates in Pt/Vulcan carbon!

Quaternary α-phase



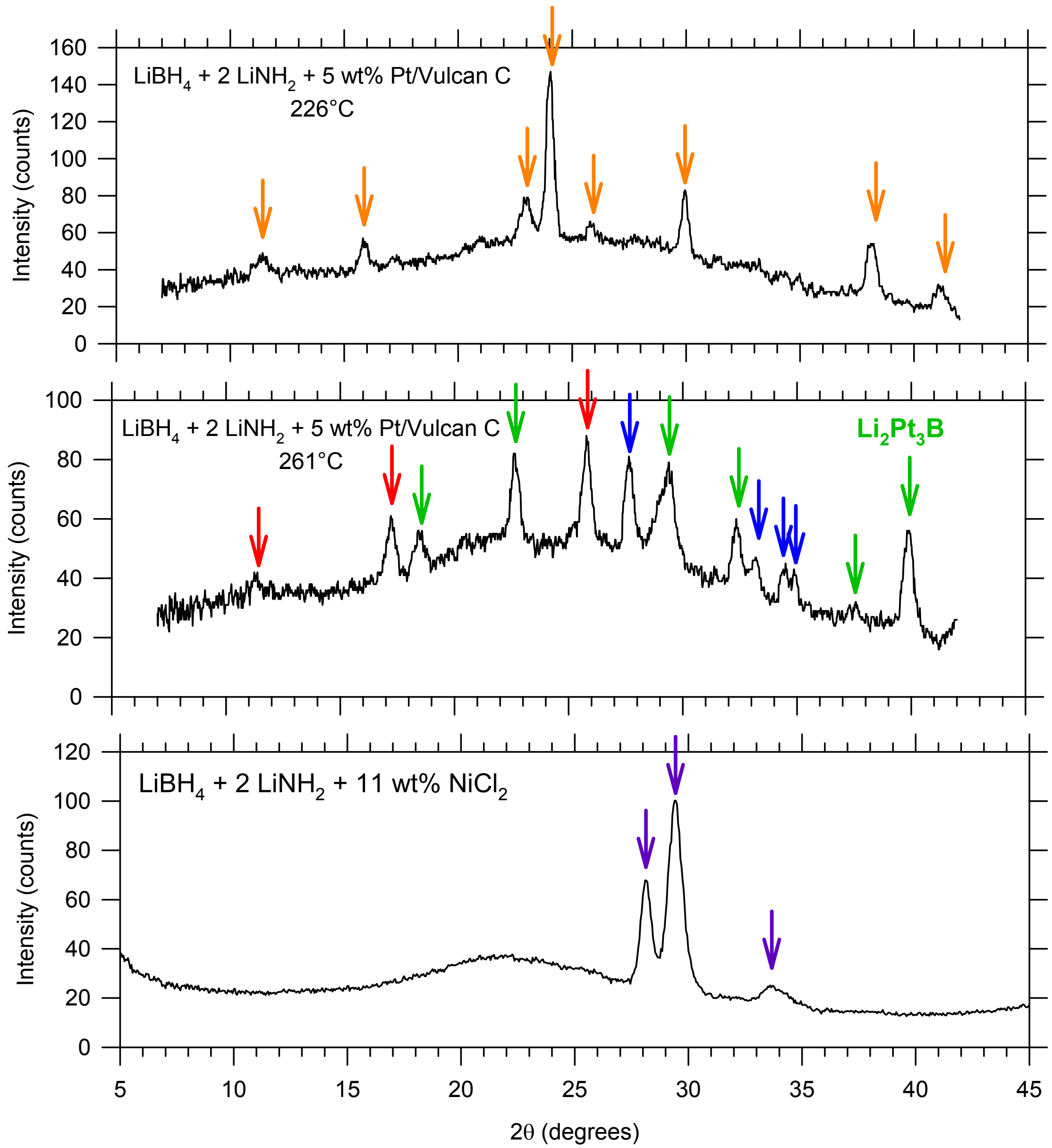
Pinkerton et al., JALCOM, available online.

Comparison of intermediate phases

Pt/Vulcan carbon
Intermediate 1
(226°C)

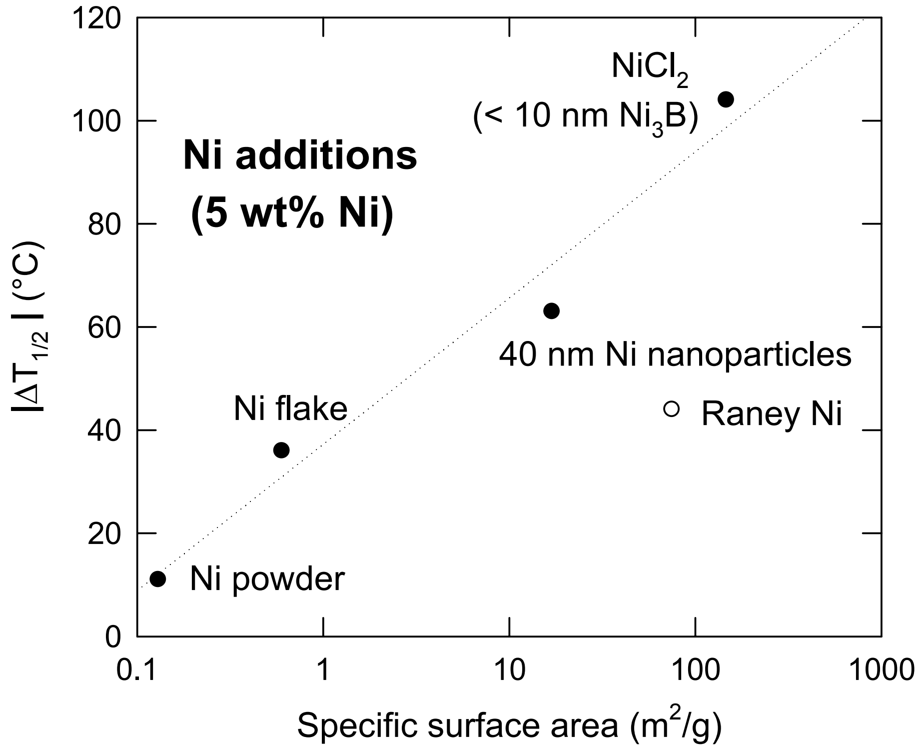
Pt/Vulcan carbon
Intermediate 2
(261°C)

$NiCl_2$
Intermediate
(~210-~290°C)



What are the additives doing?

- Small quantities (~1 mole%) have a large effect
- $\Delta T_{½}$ scales with the specific surface area (m^2/g) of the additive particles
- Effect appears to saturate at low addition levels (~2 mole% for $NiCl_2$)

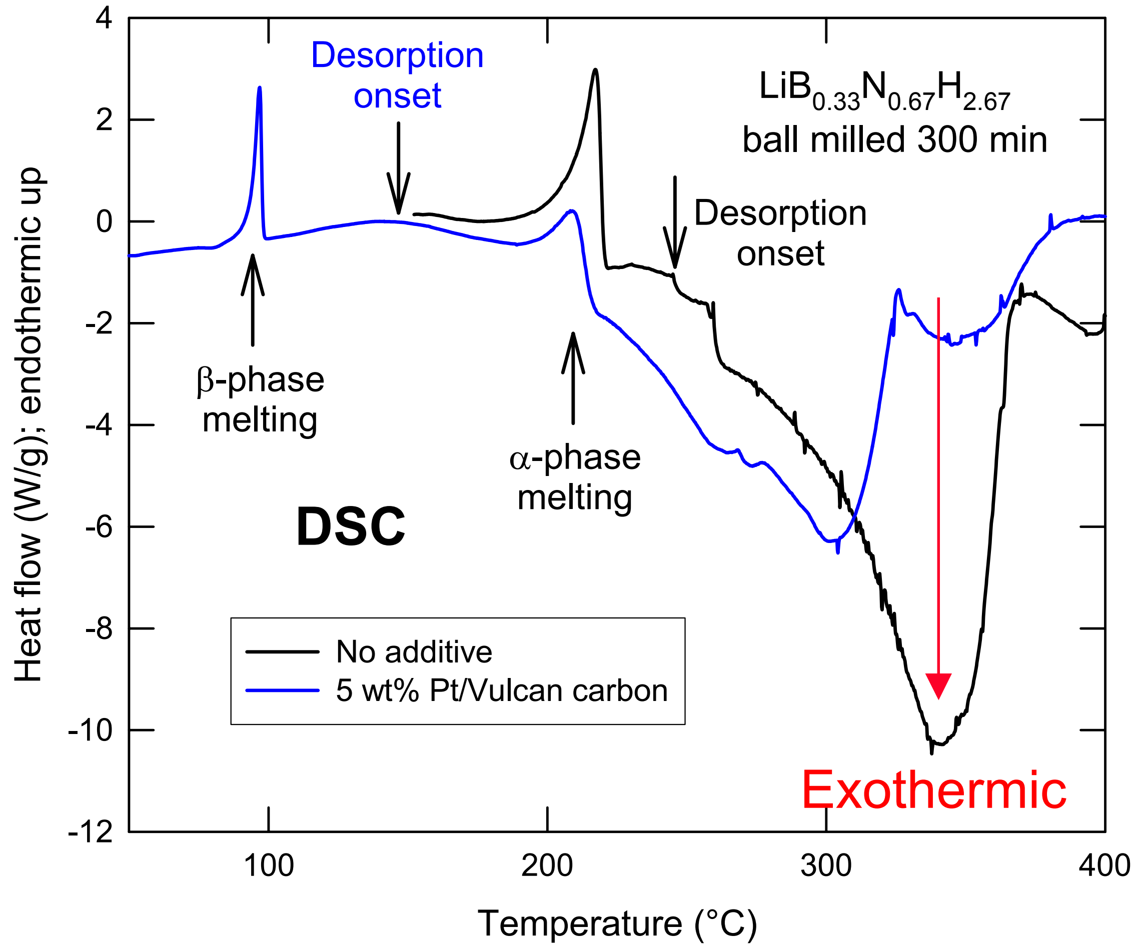


- Likely acting as a dehydrogenation catalyst

What about reversibility?

- Dehydrogenation appears to be exothermic
- Thermodynamically unstable
- => difficult to reverse (off-board regeneration)
- **Caveat:**

  It's not a simple system: H_2 release, NH_3 release, and Li_3BN_2 solidification are happening simultaneously



Pinkerton et al., J. Phys. Chem. B 110, 7967 (2006).

DFT estimates of reaction enthalpy

- $2\ LiNH_2 + LiBH_4 \rightarrow Li_3BN_2 + 4\ H_2$
  - **ΔH ~ 23 kJ/mol H_2** - Aoki et al., Appl. Phys. A 80, 1409 (2005)
  - **ΔH = 18-24 kJ/mol H_2** - Alapati et al., JPC B 110, 8769 (2006)
  - **Caveats:** zero T calculations *excluding zero point energy*
  - Both suggest reversibility of Li_3BN_2 to the two-phase mixture

- $Li_4BN_3H_{10} \rightarrow Li_3BN_2 + ½\ Li_2NH + ½\ NH_3 + 4H_2$
  - **ΔH = 24 kJ/mol H_2** – Herbst & Hector, APL 88, 231904 (2006)
  - Includes zero point energies and phonons: 298 K values
  - Endothermic hydrogen release suggests reversibility
  - **Caveat:** does not include α-phase melting or Li_3BN_2 solidification

- May be too unstable:
  - 1 bar H_2 equilibrium temperature is ~130-240 K

Aside:

- Reaction enthalpy for

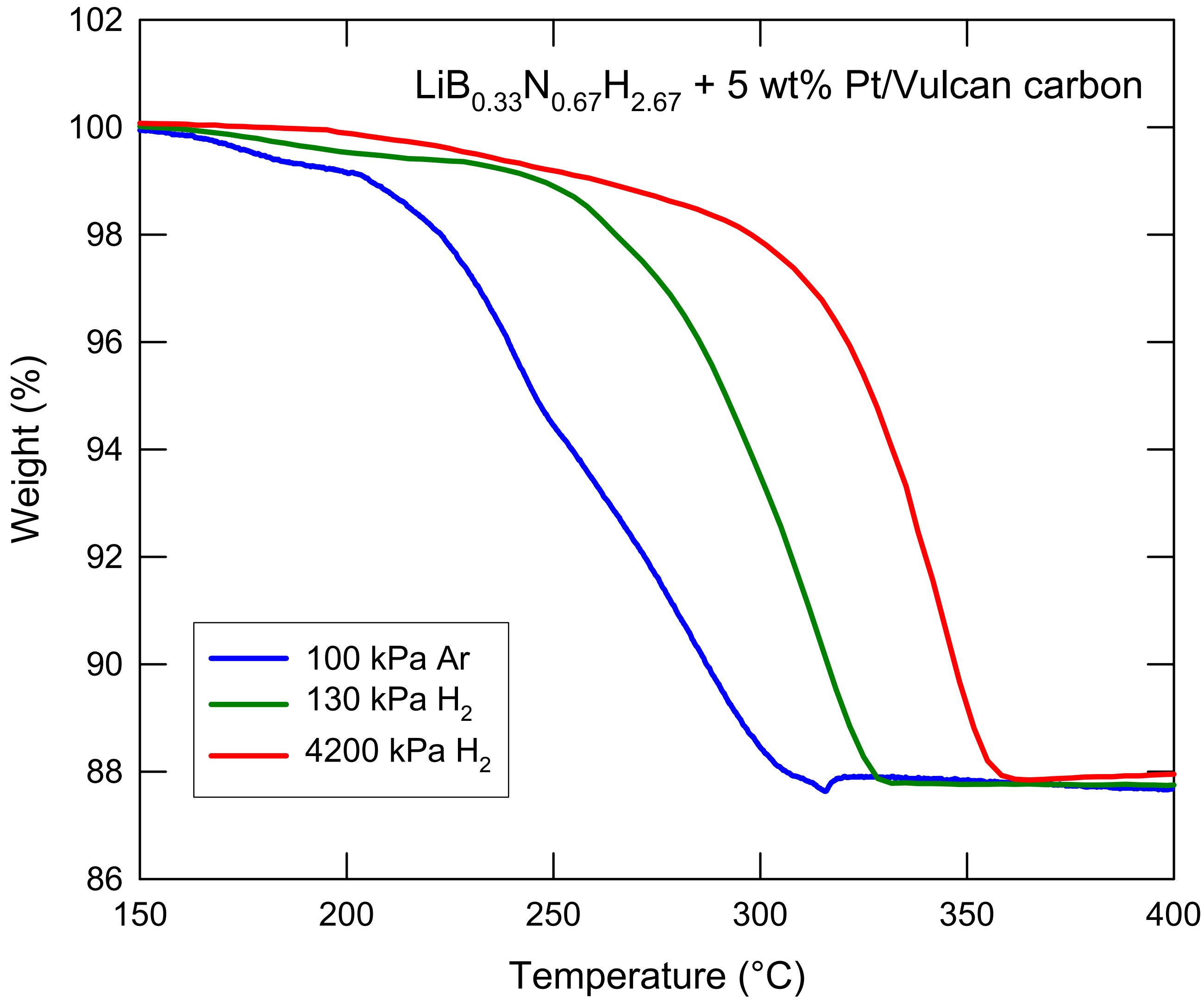
  $3\ LiNH_2 + LiBH_4 \rightarrow Li_4BN_3H_{10}$

  - **ΔH = -6 kJ/mol** – Herbst & Hector, APL 88, 231904 (2006)

- Formation of $Li_4BN_2H_{10}$ is slightly exothermic
- Consistent with observed conversion

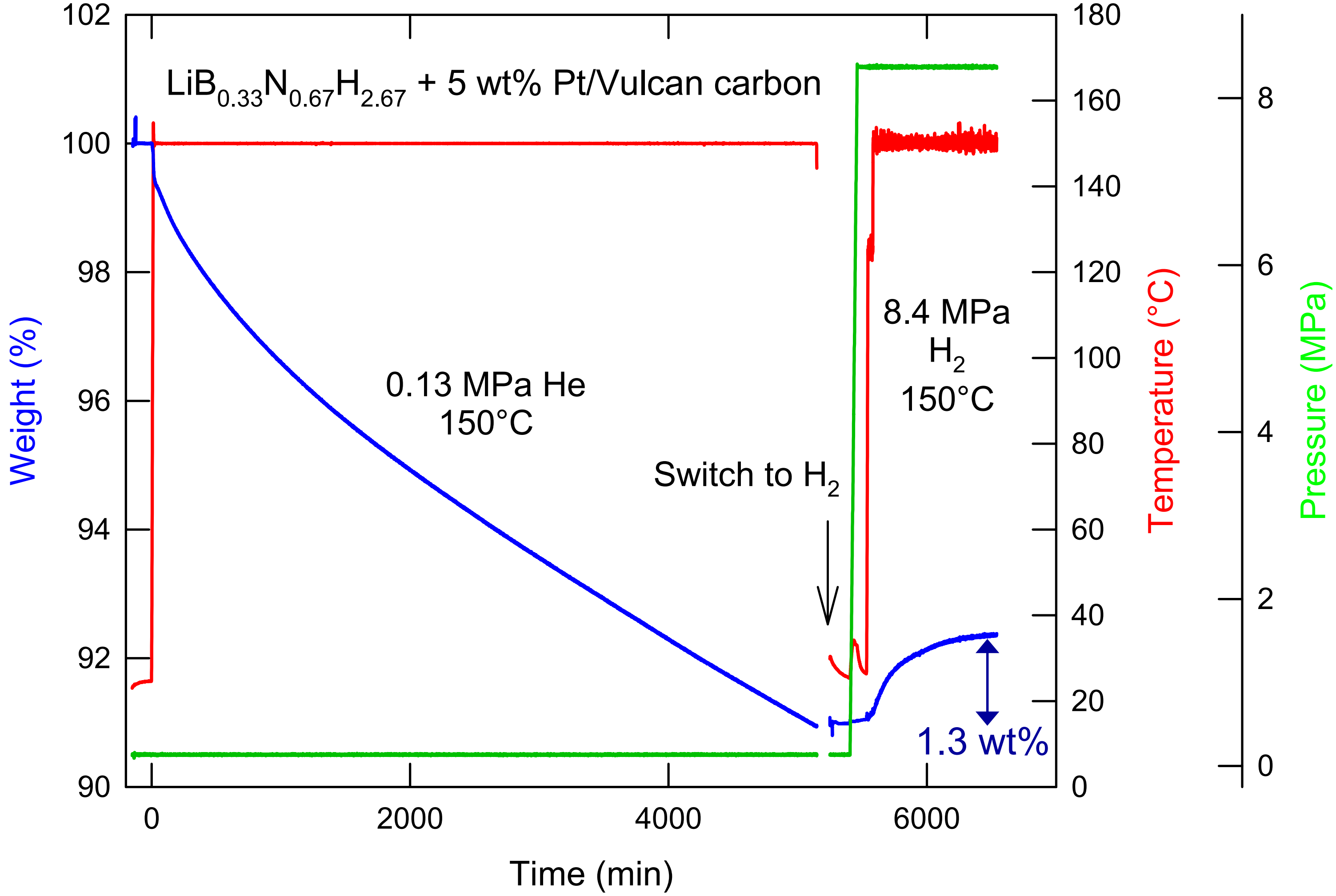
  $2\ LiNH_2 + LiBH_4 \rightarrow \alpha\ Li\text{-}B\text{-}N\text{-}H$

Effect of H_2 pressure



Pinkerton et al., J. Phys. Chem. B 110, 7967 (2006).

Attempt to rehydride $LiB_{0.33}N_{0.67}H_{2.67}$ + 5 wt% Pt/Vulcan carbon



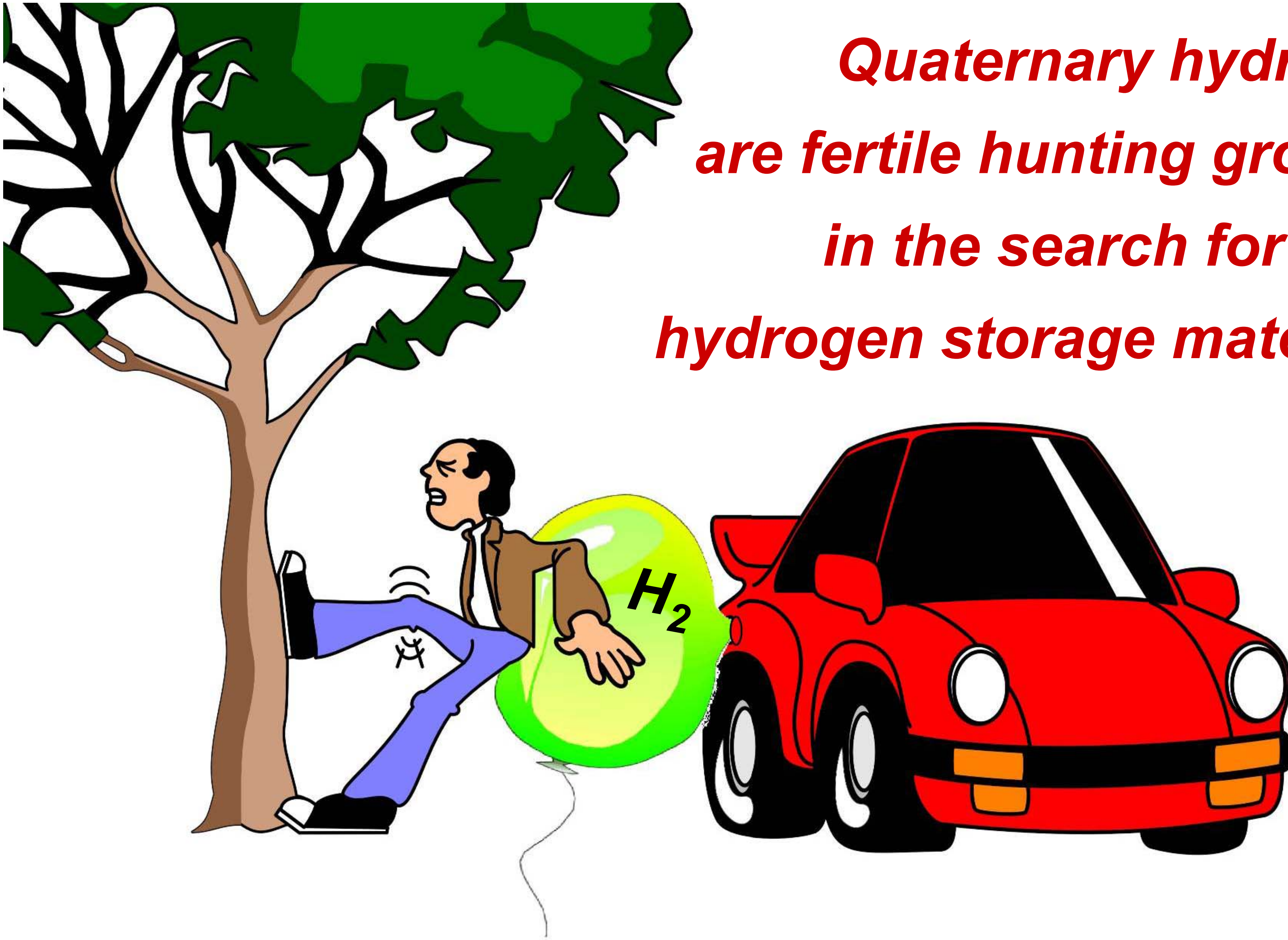
Pinkerton et al., J. Phys. Chem. B 110, 7967 (2006).

Challenges for quaternary Li-B-N-H

- Thermodynamics
  - Understand reaction enthalpies for dehydrogenation of α Li-B-N-H at different compositions
- Kinetics
  - High temperatures required to overcome slow diffusion and strong hydrogen binding and in complex hydrides
- Catalysis
  - Why does Ni or Ni_3B work so well?
  - Why *doesn't* $TiCl_3$ work?
- What if we could reduce the Li-B-N-H hydrogen release temperature below the α phase melting temperature (similar to what was done for $NaAlH_4$)?
  - Reversibility?
  - Suppress NH_3 release?
  - More practical? (Or at least, less impractical?)

On-board hydrogen storage materials-

Quaternary hydrides are fertile hunting ground in the search for new hydrogen storage materials



Summary

- **Strategy of looking for hydrogen-free products has been successful**
- **We have discovered a new quaternary hydride, α Li-B-N-H ($Li_4BN_3H_{10}$), that releases all of its hydrogen above 250°C**
  - H_2 and NH_3 release are strong functions of composition, with optimum H_2 release near $(LiNH_2)_{0.67}(LiBH_4)_{0.33}$ [2:1]
- **Numerous other Li-B-N-H phases exist**
  - 4 phases along the $(LiNH_2)_x(LiBH_4)_{1-x}$ tie line (2 metastable)
  - 4 additional phases during Li-B-N-H decomposition with additives
  - 3 more phases have been found in the Li-B-N-H phase diagram (Torgersen et al., MRS 2004 Fall Meeting)
- **Metal nanoparticle additions reduce the dehydrogenation temperature by up to 112°C ($NiCl_2$)**
- **Quaternary hydrides are fertile hunting ground in the search for new hydrogen storage materials**