Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity

S. M. Opalka, X. Tang, D. A. Mosher, B. L. Laube, R. J. Brown
United Technologies Research Center

F.-J. Wu
J. Strickler
Albemarle Corporation

P. A. Berseth
D. L. Anton
R. Zidan
Savannah River National Laboratory

B. C. Hauback
H. W. Brinks
O. M. Løvvik
Institute for Energy Kjeller, Norway

W. Huang
C. Qiu
G. B. Olson
QuesTek, LLC/ Northwestern U.

DOE Hydrogen Program

Annual Peer Review
Arlington, VA
May 16, 2007

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

- **Timeline**
  - 11/30/02 Start
  - 8/31/07 End
  - 95% Complete
- **Budget**
  - $2.9M Total Program
    - $2.1M DOE
    - $0.8M UTC & Alb.
  - $0.59M DOE FY06
  - $0.38M DOE FY07
- **Barriers/Targets Addressed**
  - System Gravimetric Capacity: 1.5 kWh/kg
  - System Volumetric Capacity: 1.2 kWh/L
  - Discharging Rate: 0.02 g/s/kW
- **Partners**
  - Albemarle Corporation
  - Savannah River National Laboratory
  - Institute For Energy - Norway
  - QuesTek, LLC

ALBEMARLE® CORPORATION

SRNL™

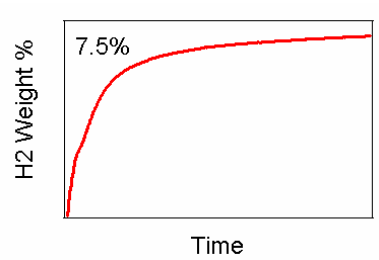
ife Institutt for energiteknikk

QUESTEK INNOVATIONS LLC

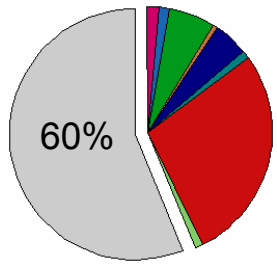
Objectives

Overall

- Develop new complex hydride compounds capable of reversibly storing H_2 with capacities $\geq$ *7.5 wt %* to meet DOE system *gravimetric* goals.



x

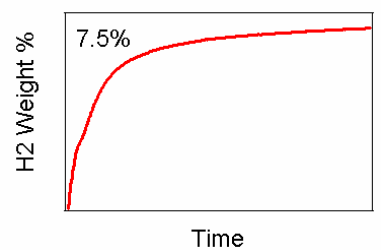


=

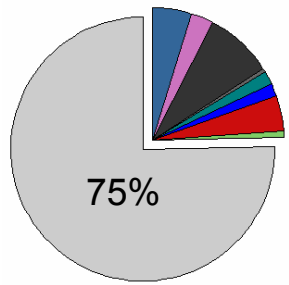
2007 Target
4.5 wt% System

- Assess potential *volumetric* capacity of new materials.

$640 \frac{kg}{m^3}$ x



x



=

2007 Target
36 kg H_2 / m^3

2006 – 2007

- Deploy integrated methods to design and optimize high H_2 capacity *mixed metal borohydrides* with and without ligand stablization.

Approach

Task / Phase	First Principles Modeling	Solid-State Processing	Solution-Based Processing	Molten-State Processing	Thermo-dynamic Modeling
2004 Known Alanates	Implement finite T predictions.	Search out quaternary systems encompassing known alkali alanates. Validate atomic-thermodynamic modeling.			Establish thermo. databases.
2005 Novel Alanates	Predict candidate properties.	Search out high capacity alanates with alkaline earth or transition metal elements. Characterize properties. Test performance.			Implement reaction design.
2006 Novel Boro-hydrides	Refine phase structure & thermo. predictions.	Synthesize high capacity borohydrides containing alkaline earths, transition metals and/or stabilized with ligands.			Design high capacity reactions.
2007 Final Phase	Probe rx. mechanisms.	Down-select best system and synthesis method. Optimize reversibility and kinetics.			Design reversibility.

Iterative design and synthesis of high H_2 capacity systems.

Program Scope

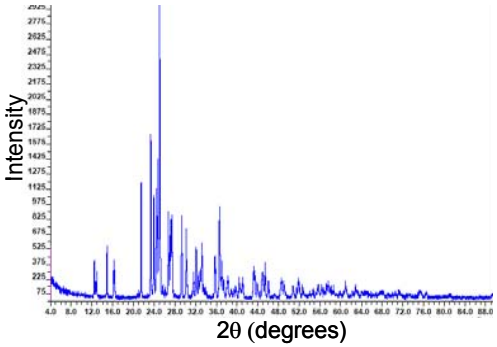
System	Compositions	Method
Alanates	Na-Li-Al-H	FPM, SSP, MSP
	Na-Tm-Al-H	FPM, SSP, SBP, MSP
	Li-Tm-Al-H	FPM, SSP, SBP, MSP
	Na-Mg-Al-H	FPM, SSP, SBP, MSP
	Li-Mg-Al-H	FPM, SSP, SBP
	Li-Na-Mg-(Ti,V,Cr,Mn,Ni,Co,Fe)-H	SSP, MSP
Borohydrides	Tm-B-H w/ ligands & coreactants	SBP
	Mg-B-H w/ & w/o ligands or coreactants	FPM, SSP, SBP, MSP
	Ak-Tm-B-H w/ & w/o ligands	FPM, SSP, SBP

UTRC/FPM – First Principles Modeling, UTRC/SSP – Solid State Processing, Albemarle/SBP – Solution-Based Processing, SRNL/MSP – Molten State Processing, Ak = alkali, Tm = transition metal

Broad range of compositions surveyed and approaches used. Ak-Tm-B-H systems are the most promising.

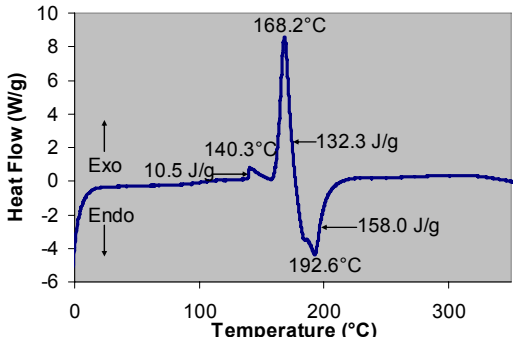
Characterization Methods

XRD



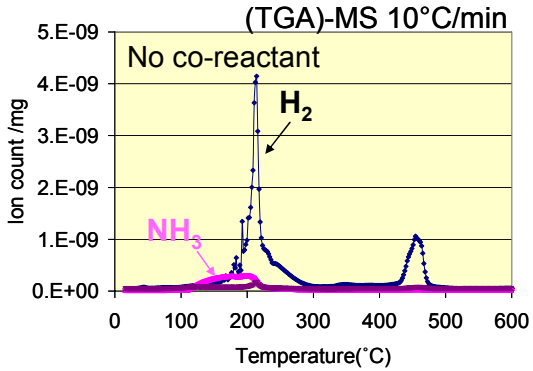
Crystalline structure & phase

DSC



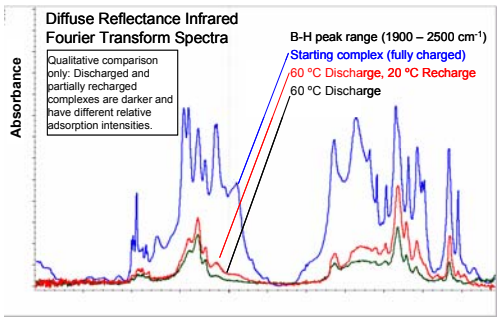
Assess reversibility potential

TGA-MS



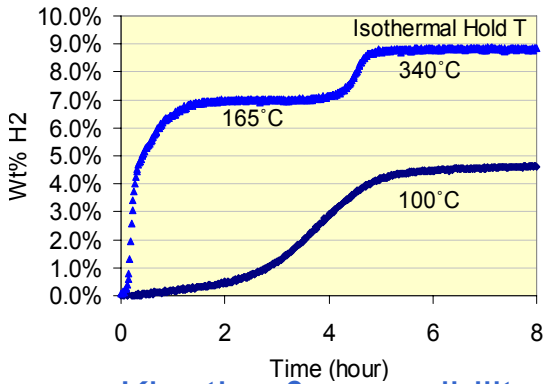
Desorption temperature & species

DRIFTS



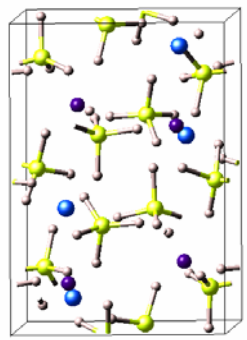
Amorphous & crystalline bond identification

PCI / Sievert's



Kinetics & reversibility evaluation

ND - IFE



Crystal / hydrogen structure

New Borohydrides – 6/2006 to Date

Ligand-Stabilized $Mg(BH_4)_2$:

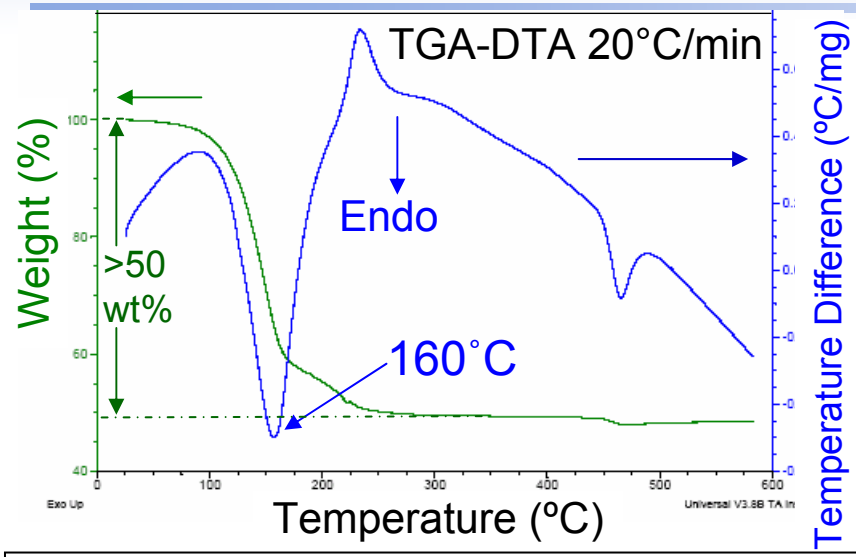
- SBP $Mg(BH_4)_2*2NH_3$ with up to **16 wt% H_2** capacity.
  SSP $Mg(BH_4)_2*3THF$ complexes also synthesized.
- Ligand complexation alters decomposition mechanism and significantly lowers dehydrogenation onset T.
- Varying complex stability observed by experiment and predicted by FPM.

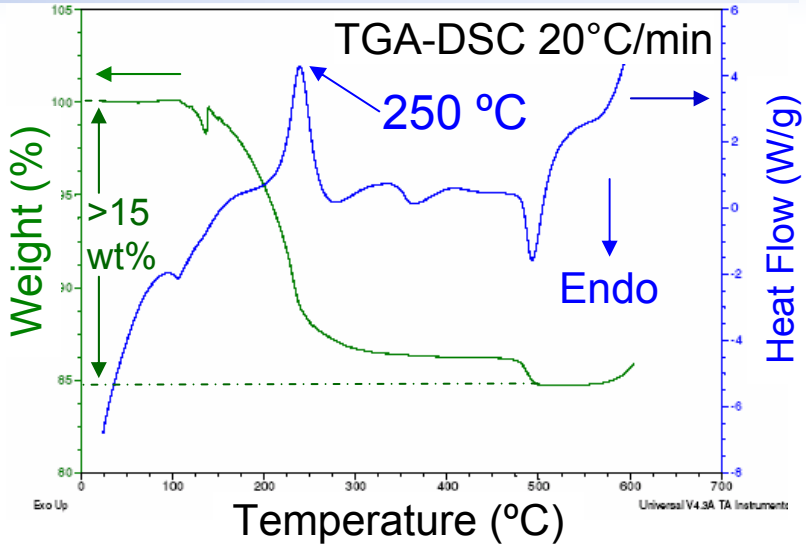
Ak-Tm-B-H (Ak = alkali, Tm = transition metal):

- Partially reversible SSP material with up to **11.7 wt% H_2** capacity.
- Ligand-stabilized SBP complexes with up to **7.3 wt% H_2** capacity.
- Metastable & stable Ak-M-B-H compositions identified by FPM.
- Continuing work with novel additives to improve Ak-Tm-B-H reversibility.

Identified multiple alkali/alkaline earth borohydrides with above target gravimetric capacities; all with issues that need resolution.

$Mg(BH_4)_2*2NH_3$ System with Up to 9 –16 wt% H_2





Hydride-NH_3 dissociation: 9 wt% H_2

Large endotherm at 100-200˚C:

$Mg(BH_4)_2*2NH_3 = Mg(BH_4)_2+2NH_3\uparrow$

Small exotherm at 200-250 ˚C :

$Mg(BH_4)_2 = MgH_2+2B+3H_2(g)$

Small endotherm at 430-470 ˚C :

$MgH_2 = Mg+H_2$

BH_3NH_3-like mechanism: 16 wt% H_2

Hydride H^- reaction with acidic H^+

Exotherm at 150-280˚C:

$Mg(BH_4)_2*2NH_3 = MgH_2+2BN+6H_2$

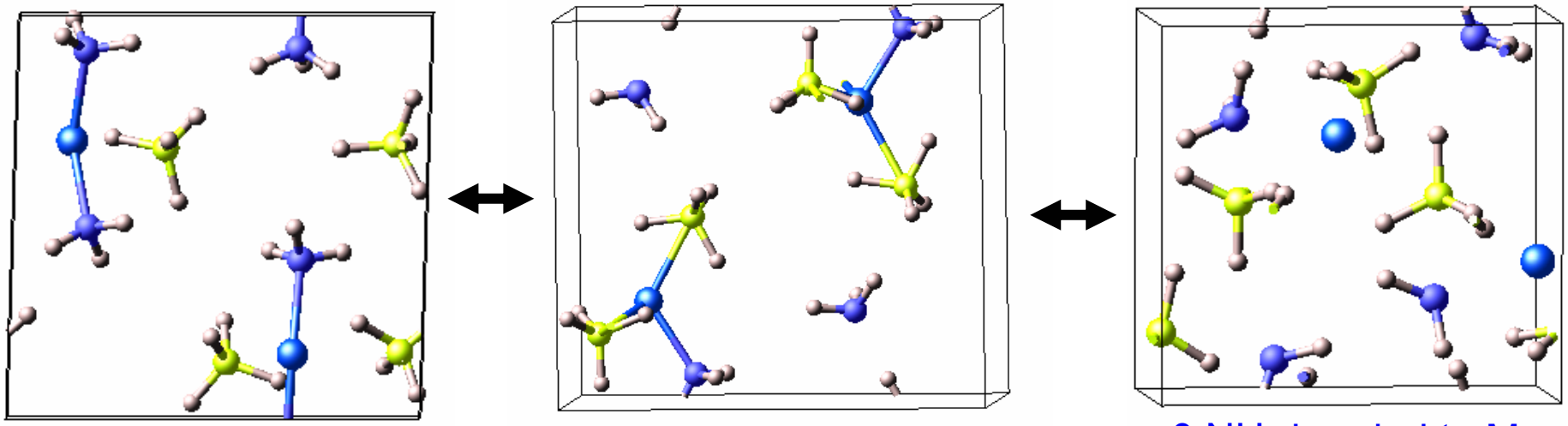
Endotherm at 480-520 ˚C :

$MgH_2 = Mg+H_2$

Coupled H_2 and ligand desorption reaction mechanisms change with processing conditions and thermal history.

Models Show Evolving $Mg(BH_4)_2*2NH_3$ Structures

More stable ⟷ Less stable



2 NH_3 bonded to Mg | 1 NH_3 bonded to Mg | 0 NH_3 bonded to Mg

$Mg(BH_4)_2*2NH_3$

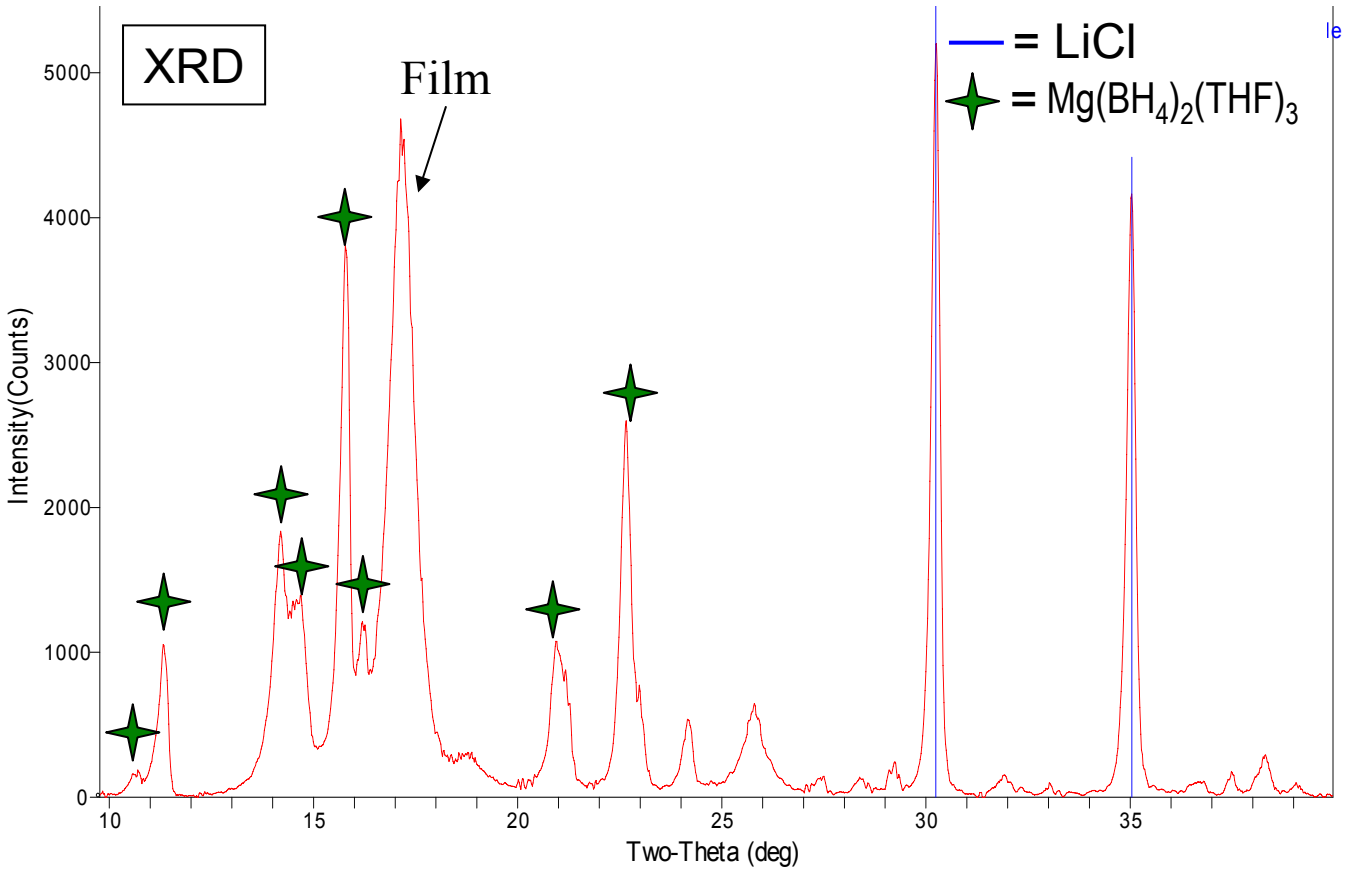
Endothermic

$MgH_2 + 2B + 2NH_3 + 3H_2$ ⟷ Intermediate reactions ⟷ $0.33Mg_3BN_3 + BN + 0.67B + 7H_2$

Exothermic

$Mg(BH_4)_2*2NH_3$ forms adducts of varying stability, exhibiting a range of decomposition reaction products and enthalpies.

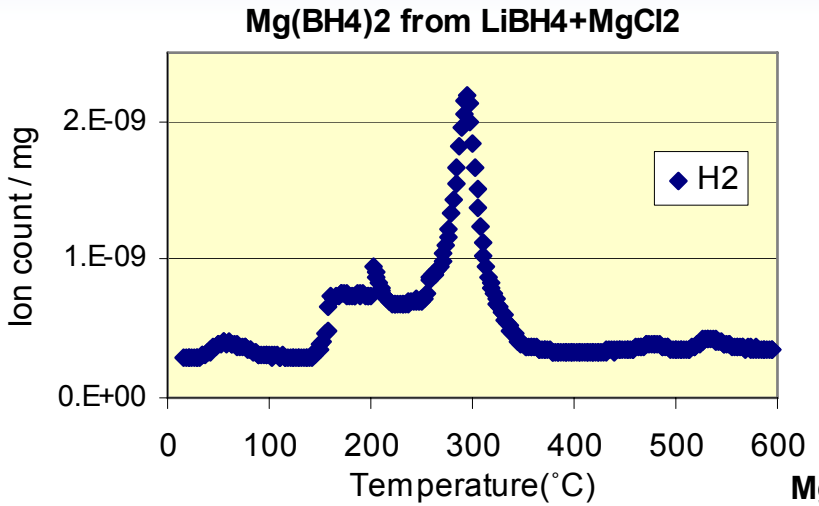
Solid-State Processing of THF-stabilized $Mg(BH_4)_2$

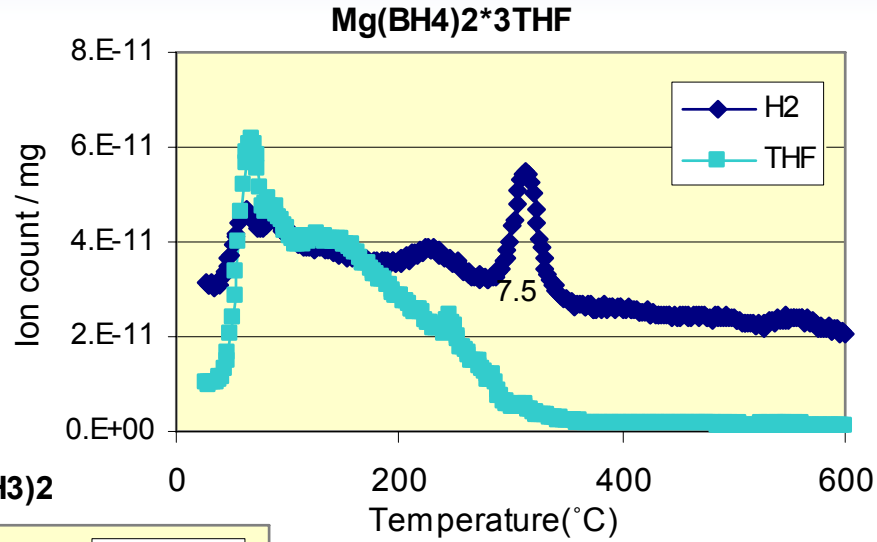


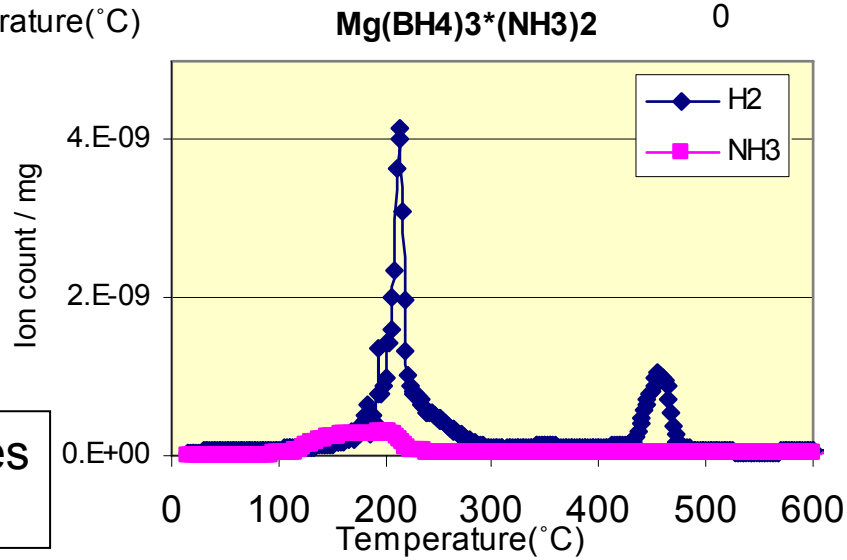
Synthesis reaction: $MgCl_2 + 2LiBH_4 + 3THF \longrightarrow Mg(BH_4)_2(THF)_3 + 2LiCl$

Identified multiple chemical routes to stabilizing $Mg(BH_4)_2$.

Mg Ligands Are a Route to Low T H_2 Release



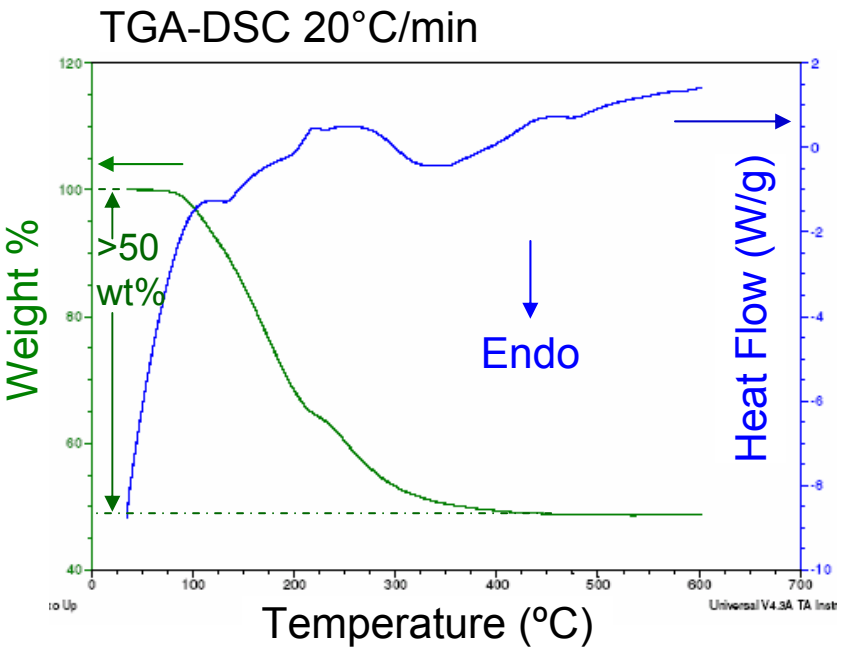


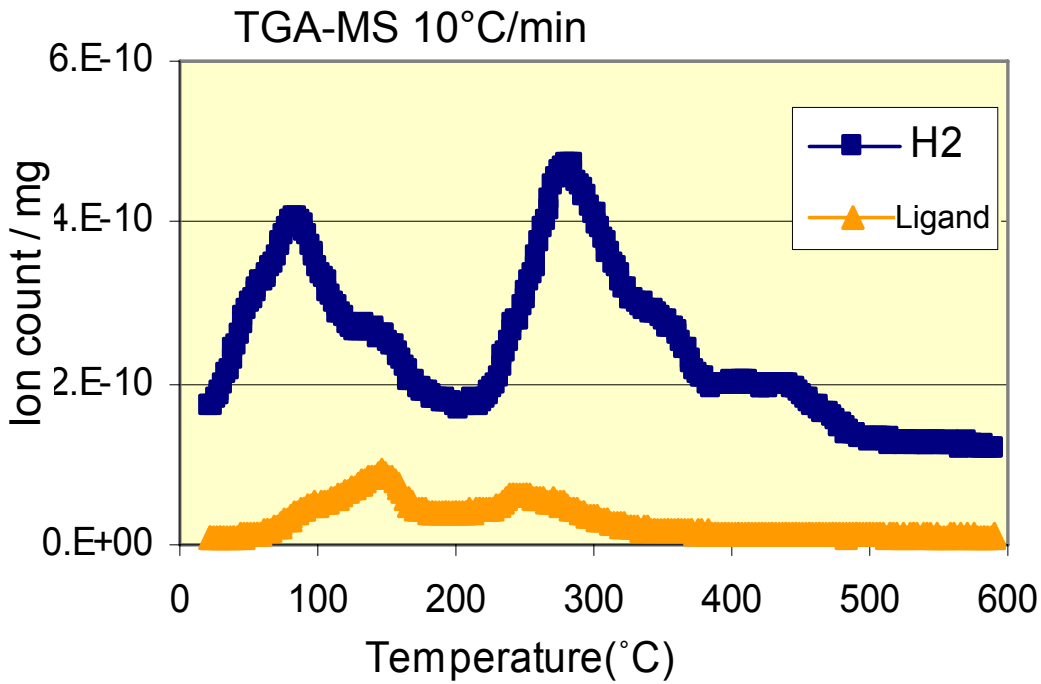


TGA / MS Analyses
All 10 ºC/min

$Mg(BH_4)_2$ complexes release H_2 & ligands starting below 300ºC.

New Aprotic $Mg(BH_4)_2$*Ligand Complex



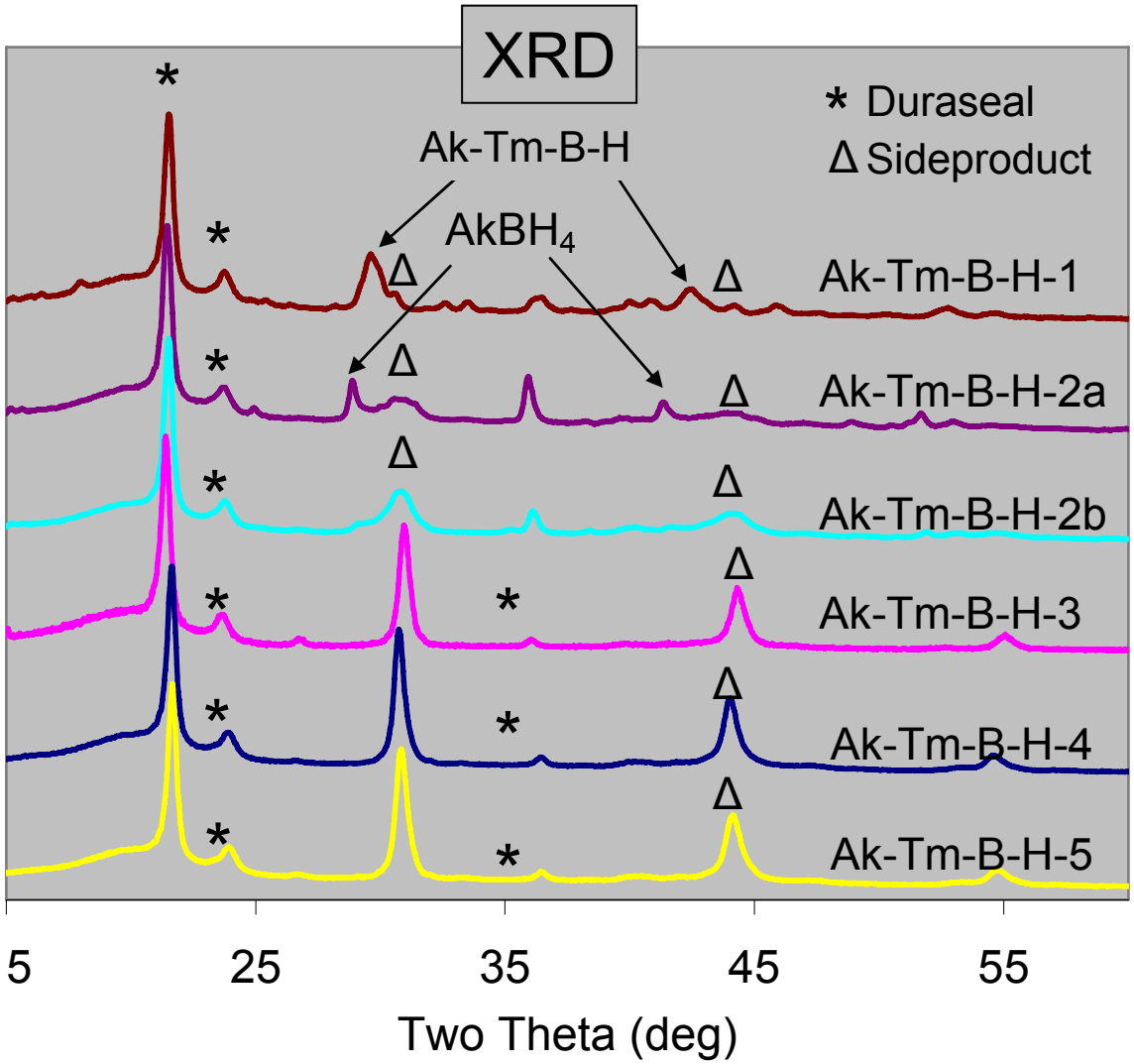


Two-stage thermal-neutral weight losses.

First stage H_2 discharge starts at 60 ºC.

Complexing ligands have a significant impact on decomposition. New ligand eliminates possible irreversible BN formation.

New Quaternary Alkali-Tm-B-H Systems

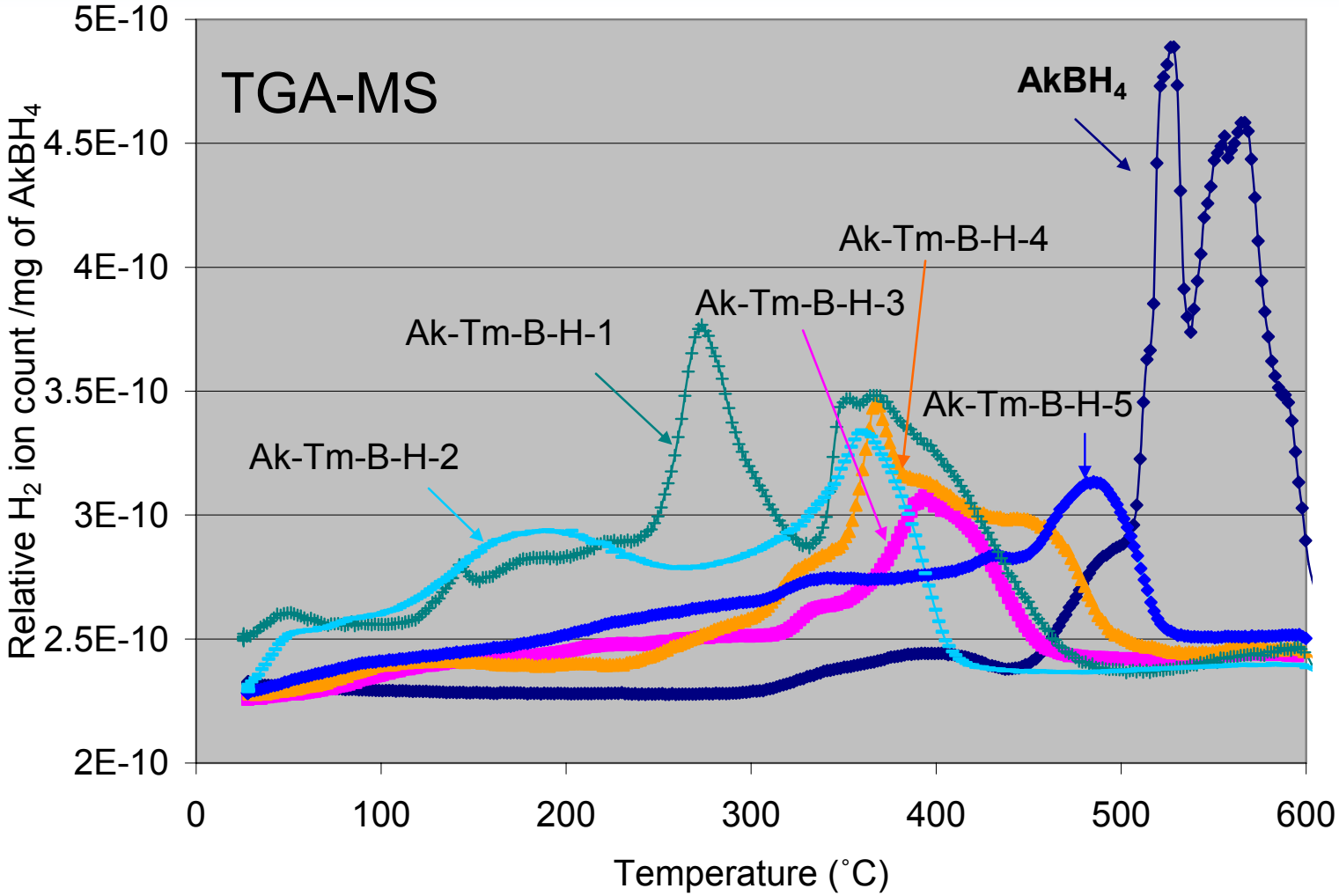


Tm addition to alkali borohydrides by SSP:

- Some outgas during milling.
- Disappearance of alkali borohydride XRD peaks.
- Mostly amorphous structure.
- Some new XRD peak formation.

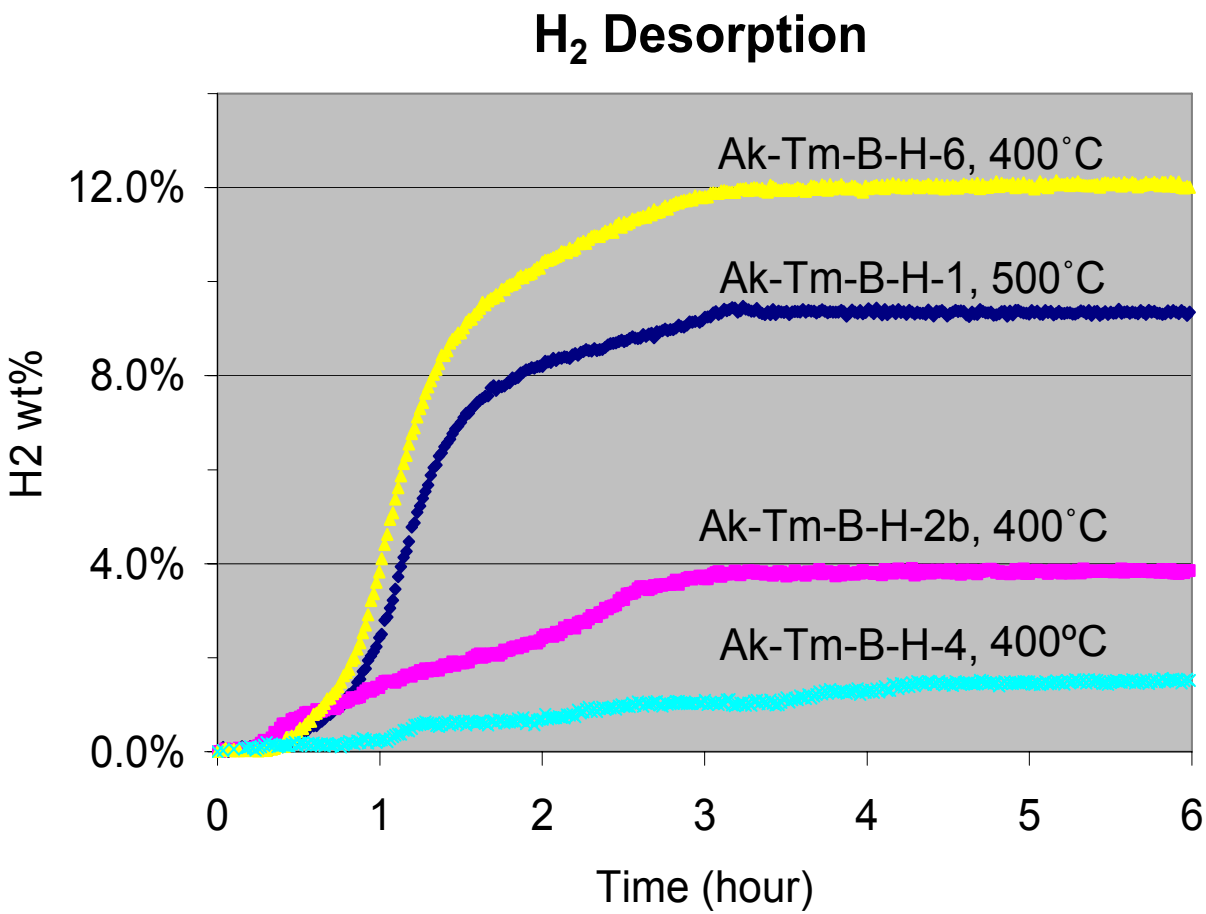
Transition metal addition disorders alkali borohydride structure.

Ak-Tm-B-H Have Up to 300ºC Lower Discharge T



Multistep reactions significantly lower dehydrogenation onset T's. Only trace B_2H_6/B_3H_9 detected in the outgas.

Partial Ak-Tm-B-H Reversibility



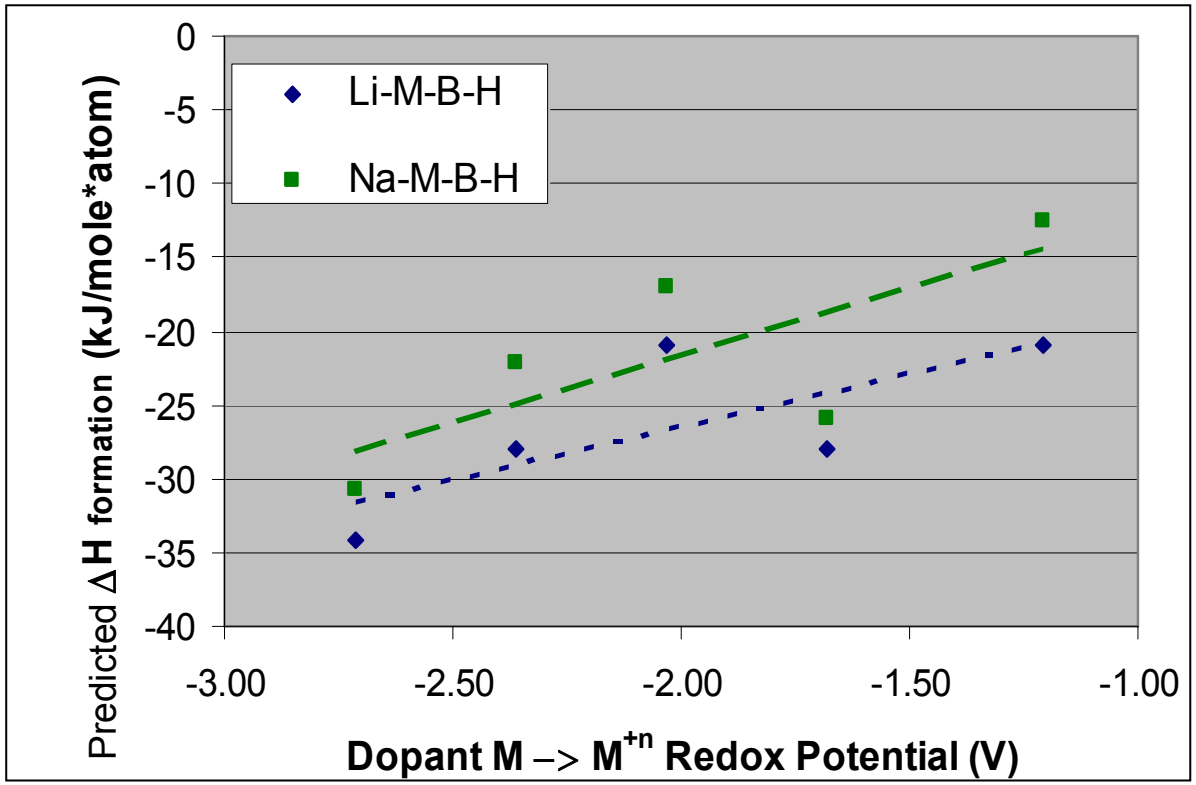
Sievert's apparatus

The H_2 wt% is calculated based on the sample weight without including removable side-products.

Ak-Tm-B-H have up to ~12 wt.% H_2 capacity. Most active composition recharged 3 wt.% H_2 at 250ºC and 195 bar H_2. Reversibility limited by Tm reduction &/or boride formation.

First Principles Survey of Ak-M-B-H Systems

Quaternaries with max. theoretical 4.9 -12.3 wt.% H_2.

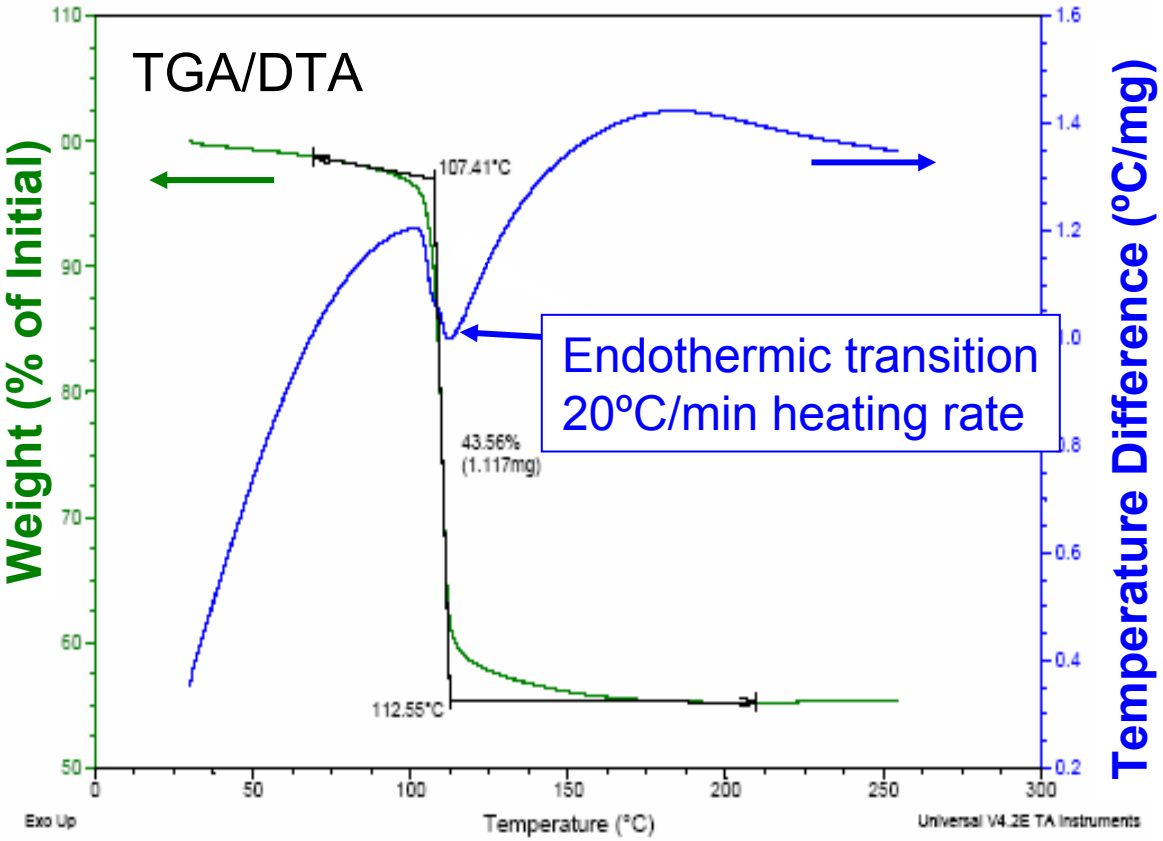


Reference Phases

Ternary Compounds	Predicted $\Delta H_{formation}$ kJ/Mol*atom
$NaBH_4$	-33.03
$LiBH_4$	-34.69
$Mg(BH_4)_2$	-23.68
$Al(BH_4)_3$	-11.98
$Ti(BH_4)_4$	-14.46

Stability of M incorporation in quaternary complex hydride phase correlates well with M electronic properties.

Ak-Tm-B-H*Ligand with Up to 7.3 wt% H_2 Endothermic



Temperature (ºC)

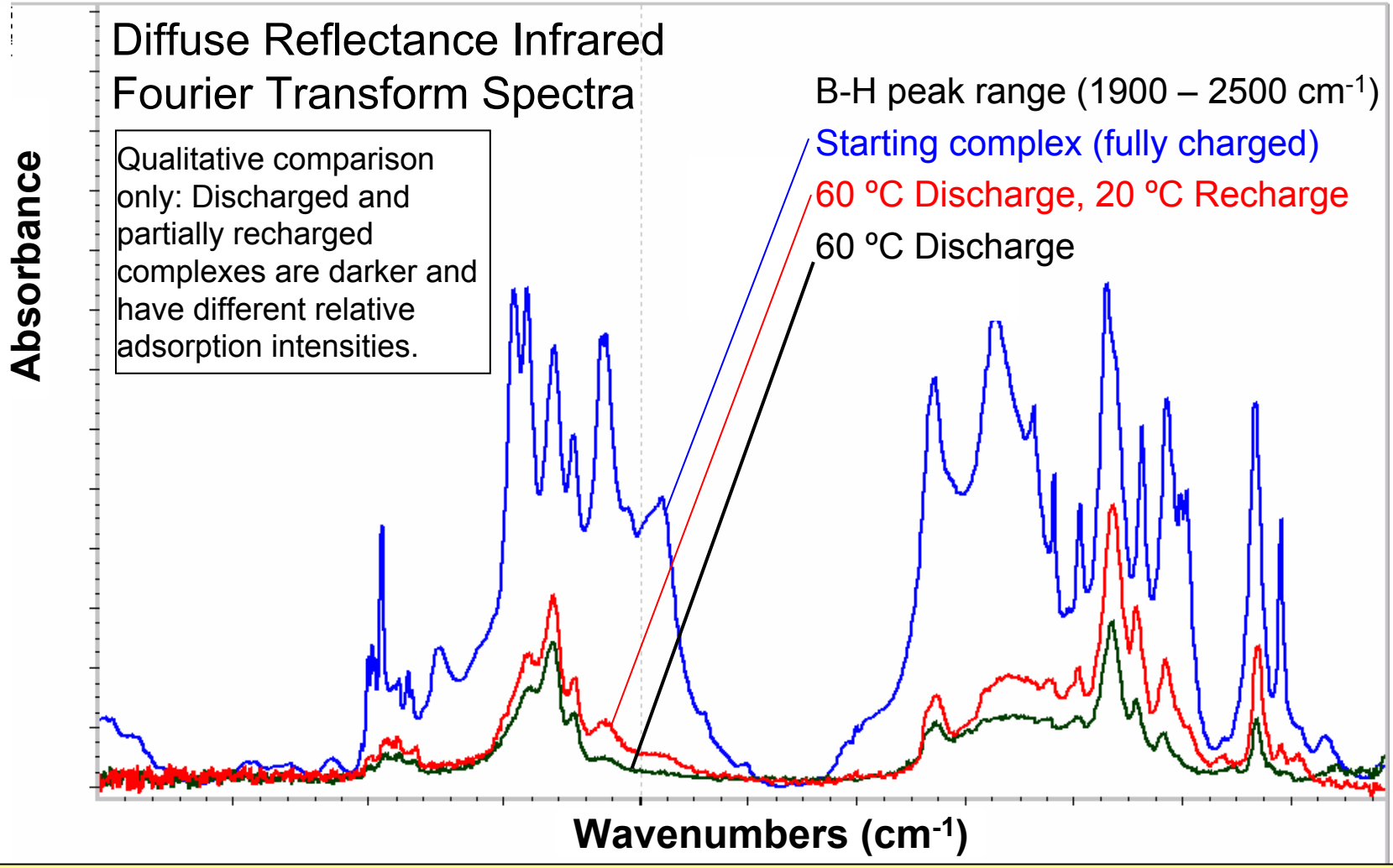
SBP Attributes:
High yield, low cost materials.

Partial H_2 discharge at 60ºC and recharge at 20ºC.

Compare to Ti-doped $LiBH_4$ which discharges at 350ºC and recharges at 600ºC (US pat. appl. 0046930, 2006).

Fast kinetics, rapid H_2 desorption > 60 ºC without catalyst.
B_xH_y evolution below detection limit.

Ligand-Stabilized Ak-Tm-B-H Partial Reversibility



DRIFTS analyses show evidence for partial rehydrogenation, probably limited by irreversible product formation.

Summary of Materials Discovery to Date

1) **Compositional surveys** of >**9** quaternary systems

2) **Theoretical methods** - coupled complex reaction design.

3) **Synthesis & characterization** of high capacity materials with > 7.5 wt% H_2 & up to 0.04 kg H_2/L:
$LiMg(AlH_4)_3$ | Mg-B-H-Ligands | M-B-H-Ligand A &-Ligand B

4) **Discovery** of low T, partially reversible, up to 11.7 wt% H_2 & up to 0.04 kg H_2/L capacity $Ak_XTm(BH_4)_Y$ materials.
* H_2 with only trace B_xH_y from SSP material.
* Good kinetics for SBP material.

5) **Identification** of stable and metastable constituents for optimizing quaternary Ak-M-B-H capacity and reversibility.

Lessons Learned

Integration of FPM, syntheses and characterization is a successful paradigm for screening, testing and mechanistic understanding of new materials.

Syntheses often leads FPM in material discovery. Multiple synthesis methods maximize opportunities for material discovery. Unique FPM insights guide and focus experimentation for material design and optimization.

FPM yields greatest value when iteratively coupled with experiments for the:

- Determination of new material structures and properties and
- Investigation of experimentally observed material behavior,

and for surveying hypothetical, lesser known or unstable material properties.

Future Work

- Complete evaluation of hydrogen release mechanisms from $Mg(BH_4)_2$*ligand complexes.
- Complete optimization of reversibility of Ak-Tm-B-H system.
- Final contract reporting and publications.

Summary Table

Progress Toward Hydrogen Storage System Targets*				
Target	**Units**	**2007 System Targets**	**'05 to '06 Best Alanate $LiMg(AlH_4)_3$ / System**	**'06 to '07 Best Borohydride $Mg(BH_4)_2*2NH_3$ / System**
Gravimetric Capacity	kWh/kg (kg H_2/kg)	1.5 (0.045)	2.1 / 1.3 (0.070 / 0.042)	3.0 / 1.8 (0.091 / 0.055)
Volumetric Capacity	kWh/L (kg H_2/L)	1.2 (0.036)	0.5 / 0.38*** (0.015 / 0.011)	1.5 / 1.1 (0.044 / 0.033)
Desorption Rate** & T	g/s/kW °C	0.02 (<100)	0.019 165	0.037 100-300

* For system design with material 60% of system mass & 75% of system volume.

** Calculated results based on 5 kg storage for 75 kW fuel cell.

*** $LiMg(AlH_4)_3$ in as received condition – ball milling could improve densification.

Gravimetric & volumetric targets are feasible, but reversibility is a challenge.