

# Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity

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**2005 DOE Hydrogen Program Review  
May 23-26, 2005  
Arlington, VA**

Project ID # ST6

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*United Technologies Research Center*

# Overview

- Timeline
  - 11/30/02 Start
  - 12/31/06 End
  - 40% Complete
- Budget
  - \$2.9 M Total Program
    - \$2.1M DoE
    - \$0.8M (27%) UTC/ALB
  - \$0.43M DoE FY'04
  - \$0.68M DoE FY'05
- Barriers
  - Gravimetric Density: 2 kWh/kg
  - Volumetric Density: 1.5 kWh/l
  - Charging rate: 1.5 kgH<sub>2</sub>/min.
  - Discharging rate: 4 gH<sub>2</sub>/sec.
  - Safety: Meets or exceeds applicable standards
  - Durability: 1000 cycles
- Partners
  - SRNL
  - IFE
  - Albemarle
  - QuesTek LLC



# *Objectives*

## **Total Program Objectives**

To develop **new complex hydride compounds that can:**

- Reversibly store  $\geq 7.5$  weight % capacity,
- Discharge H<sub>2</sub> at rates required for PEM fuel cell operation,
- Recharge for 1000 cycles with 100 % recovery.

## **First Year (2004) Objectives**

- Implement and validate new atomic-thermodynamic predictive methods.
- Search out quaternary systems for high H capacity candidates formed from Na, Li, Ti, and/or Mg combined with Al and H, using multi-pronged approach:

**Atomic-Thermodynamic Modeling**

**Solid State Processing (SSP)**

**Molten State Processing (MSP)**

**Solution Based Processing (SBP)**

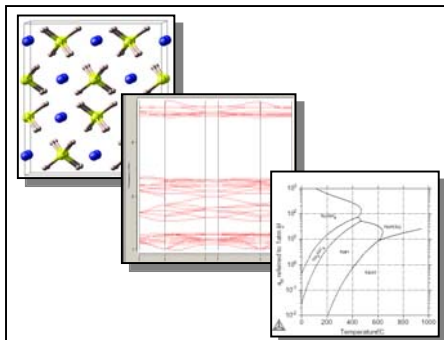
# Approach

## Virtual and Experimental Processing Methods

Discover reversible high H compounds,  $Ak_x Ae_y M^+{}_z (AlH_4)_{(x+2y+iz)}$ , formed between alkali (Ak) and alkaline earth (Ae) hydrides, metals (M),  $AlH_3$ , and  $H_2$ .

### Atomic-Thermodynamic Modeling (UTRC)

- Survey broad compositional spaces
- Supplement thermodynamic data
- Generate descriptions of phase behavior



### Solid State Processing, SSP (UTRC)

- Very rapid, low cost screening
- Limited conditions
- High cost for high volume production



### Molten State Processing, MSP (SRNL)

- Rapid screening
- Wide range of T & P
- Includes metastable phases
- Expensive equipment



### Solution Based Processing, SBP (Albemarle)

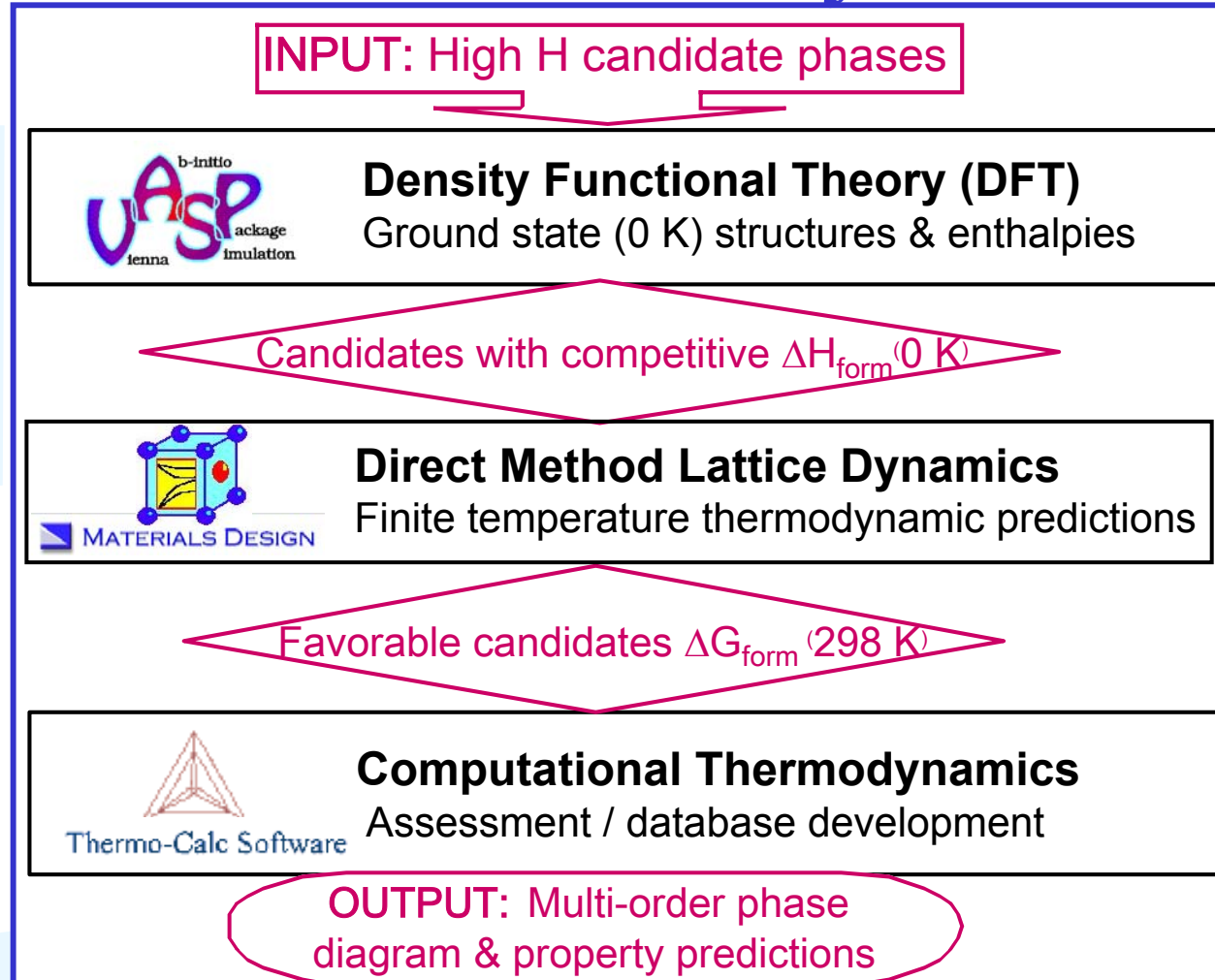
- Excellent control
- High purity products
- Expensive processing
- Cost-effective high volume production



Unique aspect of approach: utilize a wide range of modeling and synthesis methods to search out and discover new high  $H_2$  capacity systems.

# Accomplishments:

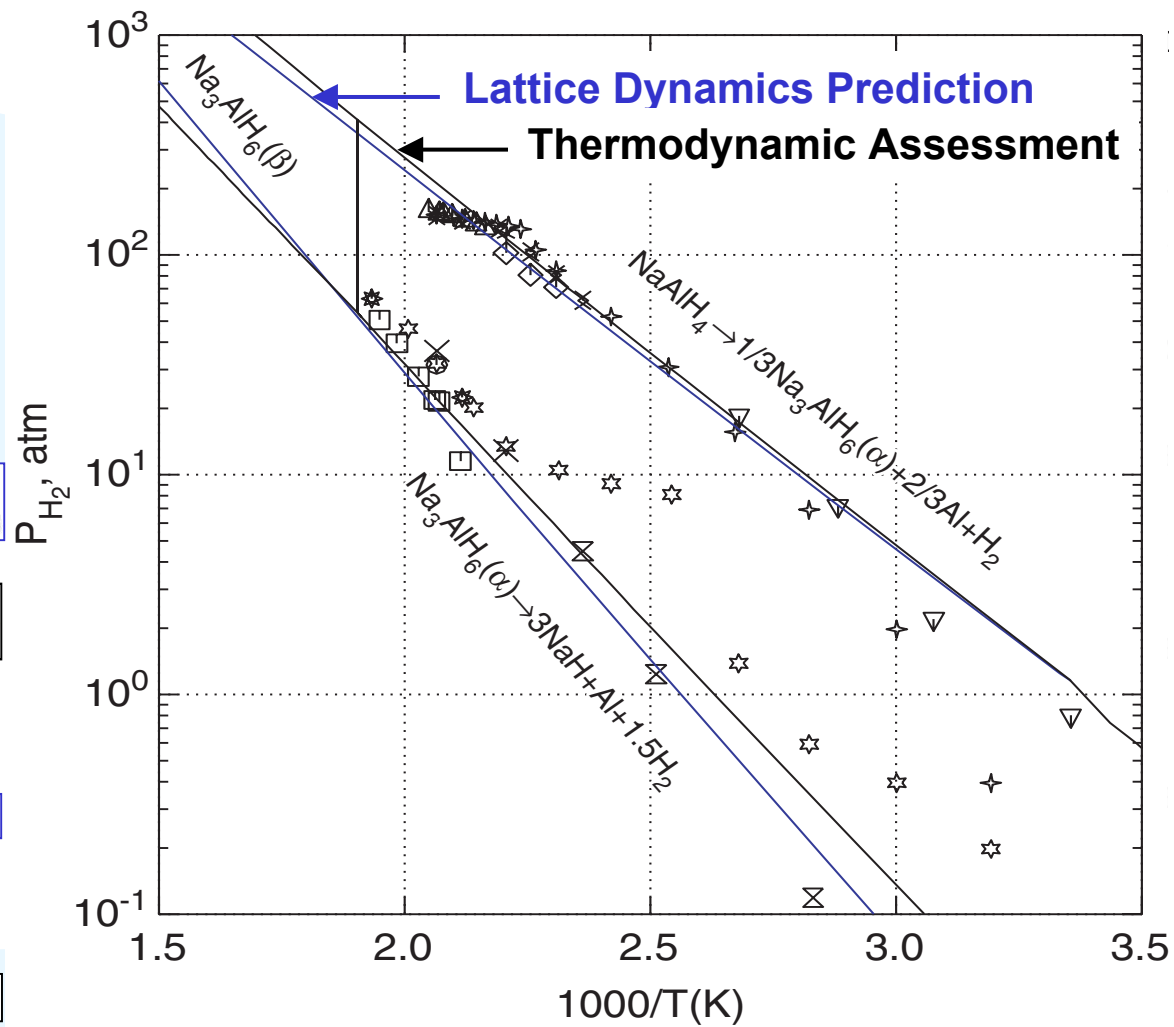
## Established Atomic-Thermodynamic Flowpath



Coupled methodologies provide the capability to discover and evaluate high H capacity candidates' thermodynamic phase behavior, prior to experimentation.

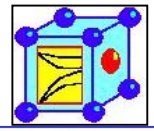
# Accomplishments:

## Validation of First Principles (FP) Predictions



### Experimental Data

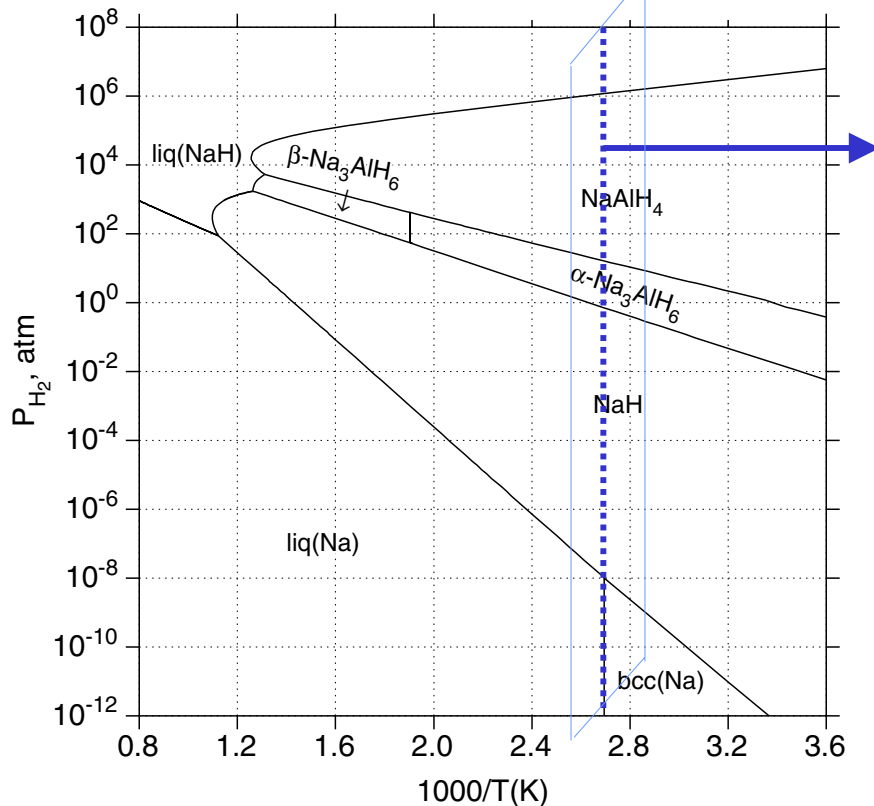
- Dymova 1974
  - $\triangle$  undoped  $NaAlH_4(\text{liq})$
  - $\square$  undoped  $Na_3AlH_6$
- Thomas 1999
  - $\diamond$  Ti-doped  $NaAlH_4$
  - $\otimes$  Ti-doped  $Na_3AlH_6$
- Gross 2002
  - $\nabla$  Ti-doped  $NaAlH_4$
- Bogdanovic 1997: PCI
  - $*$  Ti-doped  $NaAlH_4$
  - $\times$   $Na_3AlH_6$  from Ti-doped NaA
  - $\circ$  Ti-doped  $Na_3AlH_6$
- Bogdanovic 2000: PCI
  - $\times$  Ti-doped  $NaAlH_4$
  - $*$   $Na_3AlH_6$  from Ti-doped NaA
- Bogdanovic 2000: dissociation
  - $\dagger$  Ti-doped  $NaAlH_4$
  - $\star$  Ti-doped  $Na_3AlH_6$



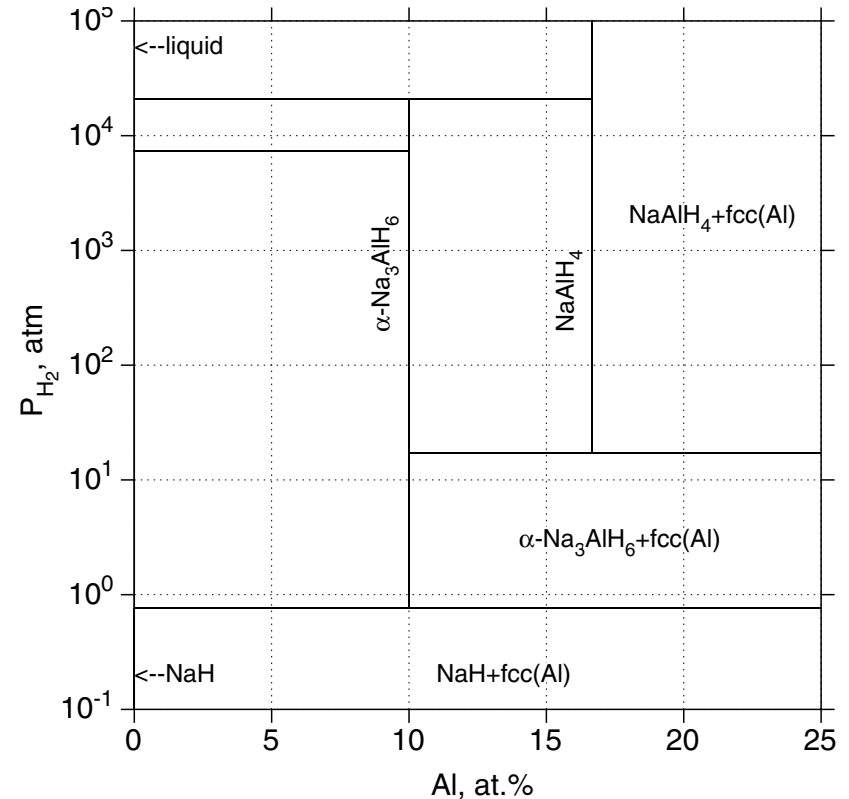
**Validation with experiment: lattice dynamic predictions in excellent agreement with thermodynamic assessment of experimental Na alate dissociation data.**

# Accomplishments: Integrated Experimental & FP Predicted Data

Potential diagram 100°C



100°C Isothermal phase section



**Predictions extend computational thermodynamics beyond experimental realm. Phase diagrams calculated from integrated assessment of experimental data and predictions used to evaluate candidate phase stability over a wide range of T & P.**



# Accomplishments:

## Virtually Surveyed Multiple Quaternary Spaces

Year II Quaternary Systems:

To Date:

Na-Mg-Al-H

Li-Mg-Al-H

Surveyed >40 Phases to date

**Identified Numerous Candidates!**

Year I Quaternary Systems:

Na-Ti-Al-H

Li-Ti-Al-H

Na-Li-Al-H

Surveyed >170 Phases

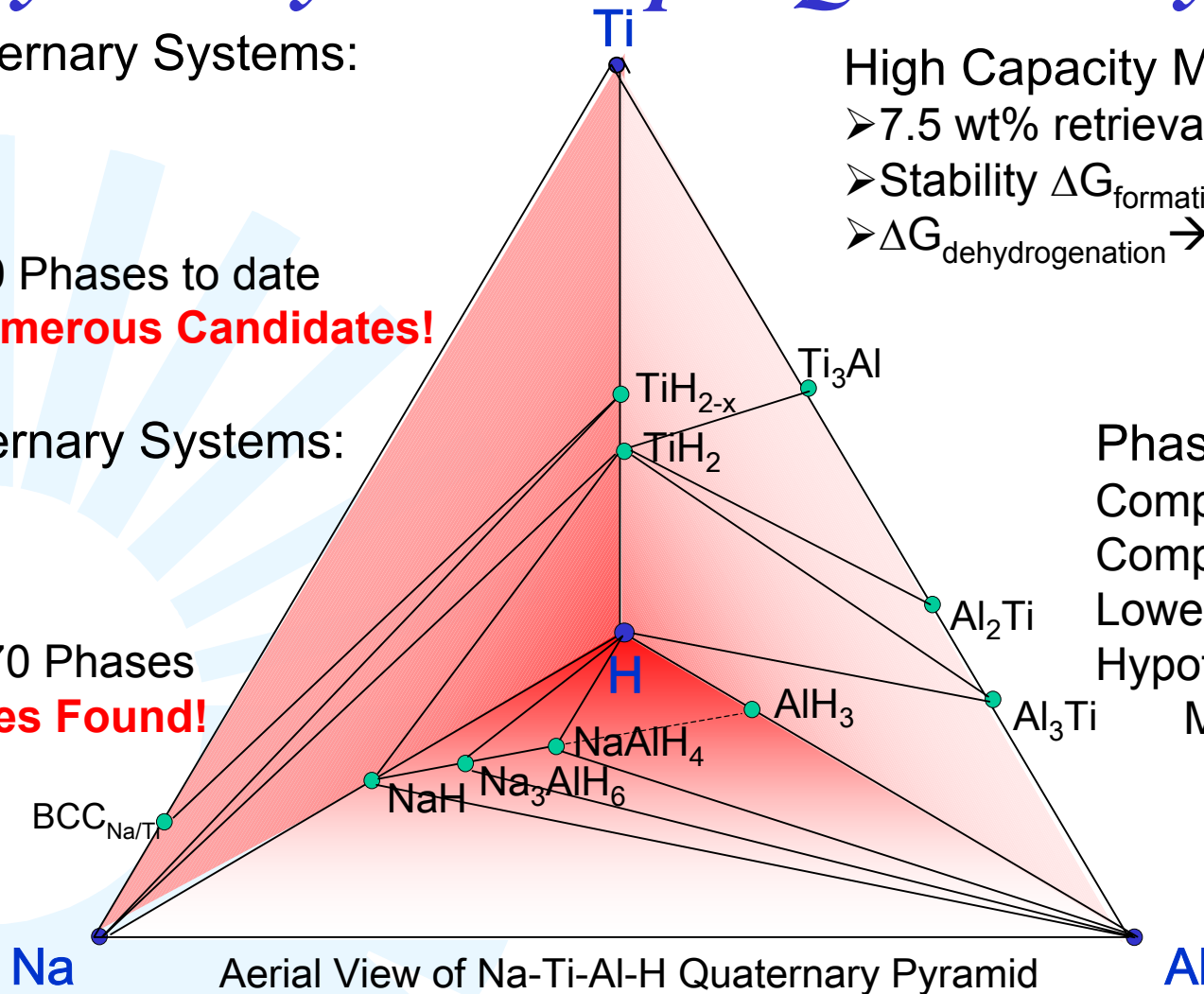
**No Candidates Found!**

High Capacity Media Criteria:

➤ 7.5 wt% retrievable H capacity

➤ Stability  $\Delta G_{\text{formation}} \ll 0$

➤  $\Delta G_{\text{dehydrogenation}} \rightarrow 0$



Phases Simulated:

Complex hydrides

Competing phases

Lower order phases

Hypothetical End-

Members

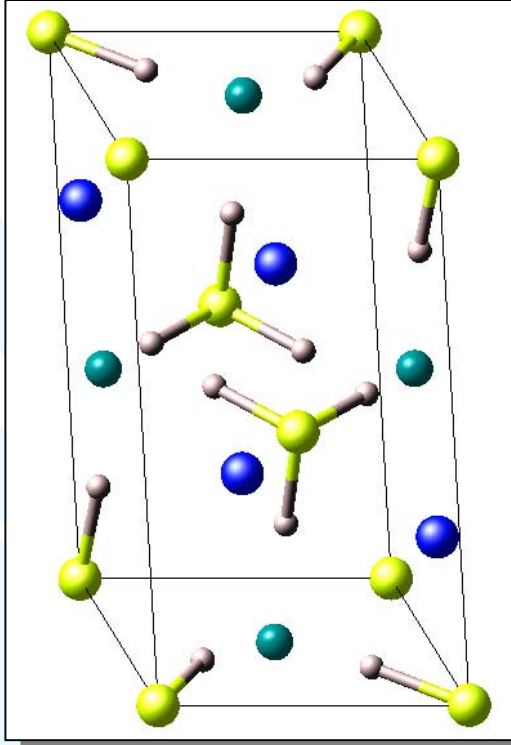


FP atomic-thermodynamic methodologies used to accelerate survey of broad compositional phase spaces, reducing and focusing experimental effort.

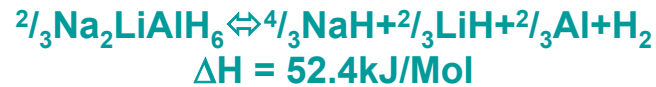
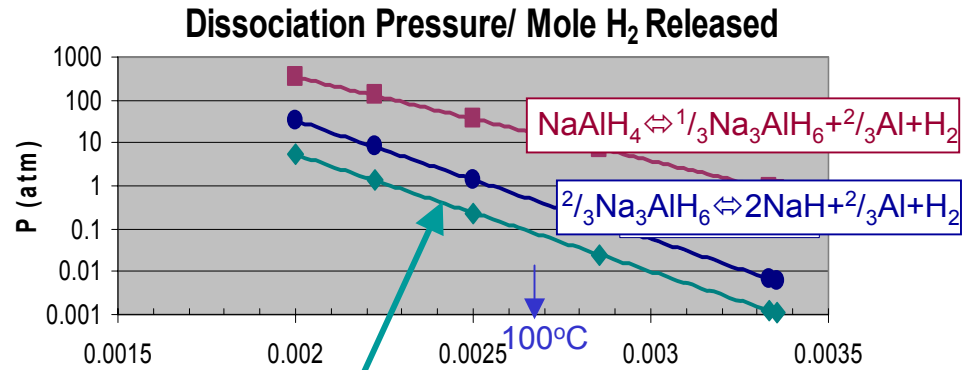


# Accomplishments:

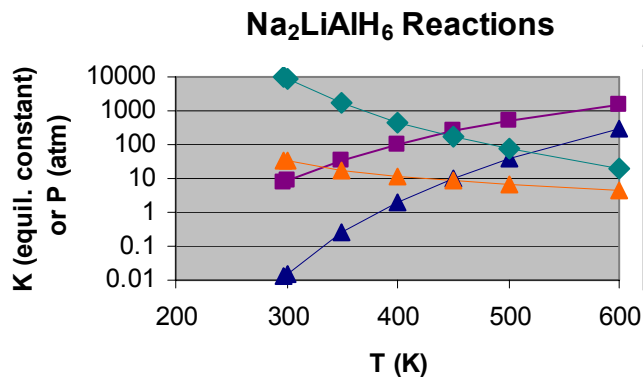
## Integrated Predictions and Experiments



Stable Low T Structure  
ID from Collaboration



Predicted and experimental (Fossdal et. al, *J. Alloys Compd., in press.*) dissociation P are in excellent agreement.



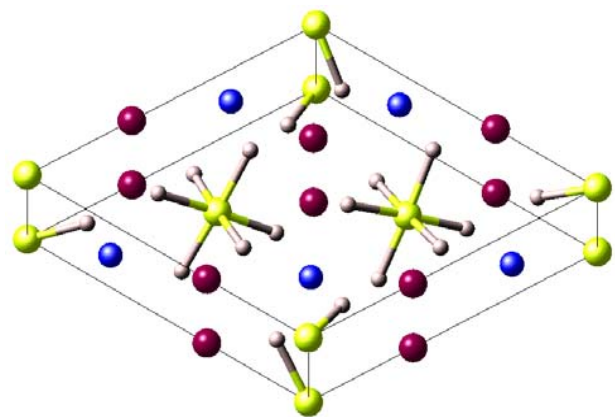
First two reactions correspond to a 2-step 5.2 w/o H<sub>2</sub> reversible system.

1<sup>st</sup>, 3<sup>rd</sup> & 4<sup>th</sup> reactions for synthesis.

Successfully employed FP predictions to evaluate Na<sub>2</sub>LiAlH<sub>6</sub> structure and phase behavior. Explained observed synthesis and disproportionation reactions.

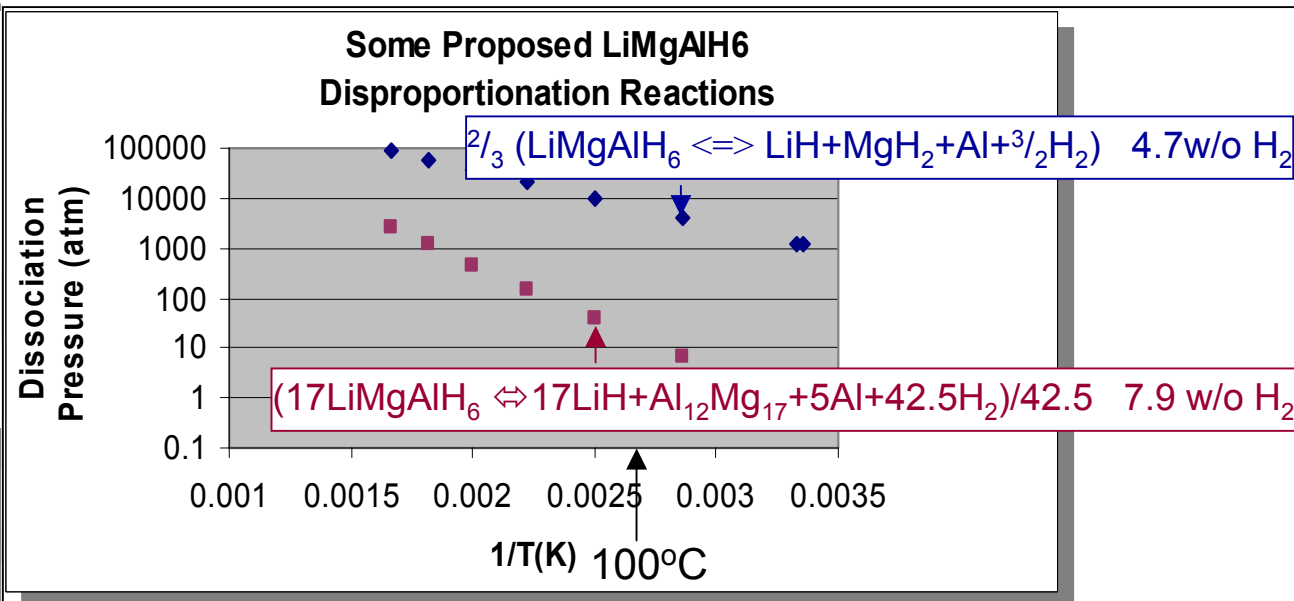
# Accomplishments:

## Identification of High Capacity Candidates



### LiMgAlH<sub>6</sub> Candidate

Many mixed alkali/alkaline earth alanate candidates predicted to have  $\Delta H_{\text{form}}(0\text{ K}) > -8\text{ kJ/mol*atom}$



Numerous possible disproportionation products are currently being evaluated. Actual reversible H<sub>2</sub> content dependent upon identification of most favorable dehydrogenation end products.

Combined predictive methodologies are effective in identifying and evaluating new candidate hydrides, yielding recommendations for experimental evaluation.

# Accomplishments

## New High H Capacity Material Search Strategy

A method of predicting destabilized alanate compounds with *in-situ* rechargeability can be described thermodynamically as:



where:

$$\Delta G \sim 0 \sim G_f^o_{M^1M^2H_i} + G_f^o_{Al} + RT \ln(P_{H_2}) - G_f^o_{M^1(AlH_4)_y} - G_f^o_{M^2H_x}$$

at  $70 < T < 120^\circ C$  &  $1 < P < 100$  bar and  $M^1$  &  $M^2$  are metal ions.

### Systematic Approach:

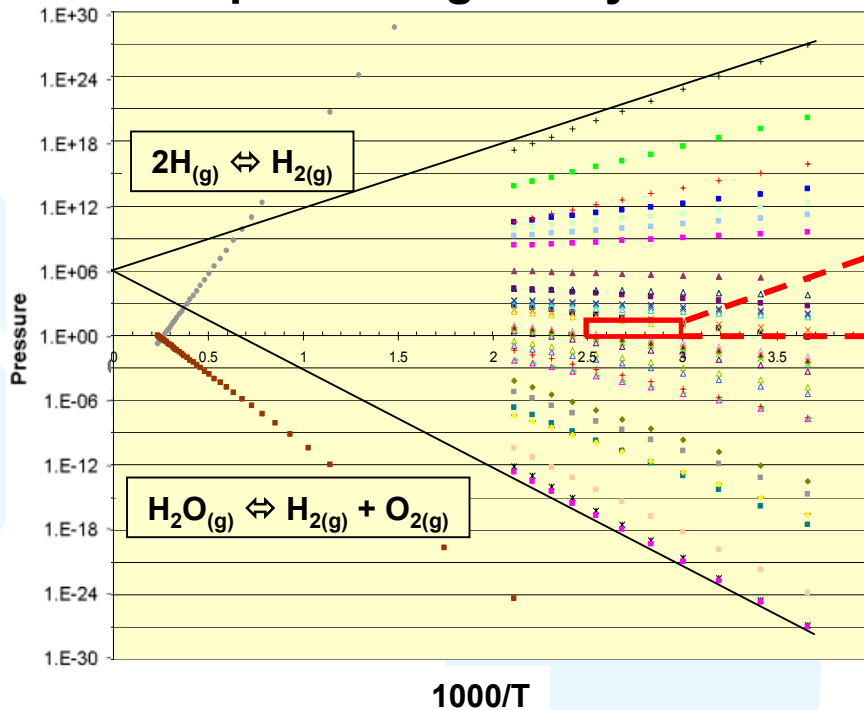
- Comprehensively search databases to select candidates from known phases.
- Identify candidate phase chemical reactions, prioritize according to  $H_2$  storage capacity.
- Where thermodynamic data is unavailable, predict thermochemical properties.
- Conduct thermodynamic assessments combining both experimental and predicted data to evaluate *in-situ* reversibility for hydrogen storage.

**New modeling tools used to select candidates for focused synthetic evaluation.**

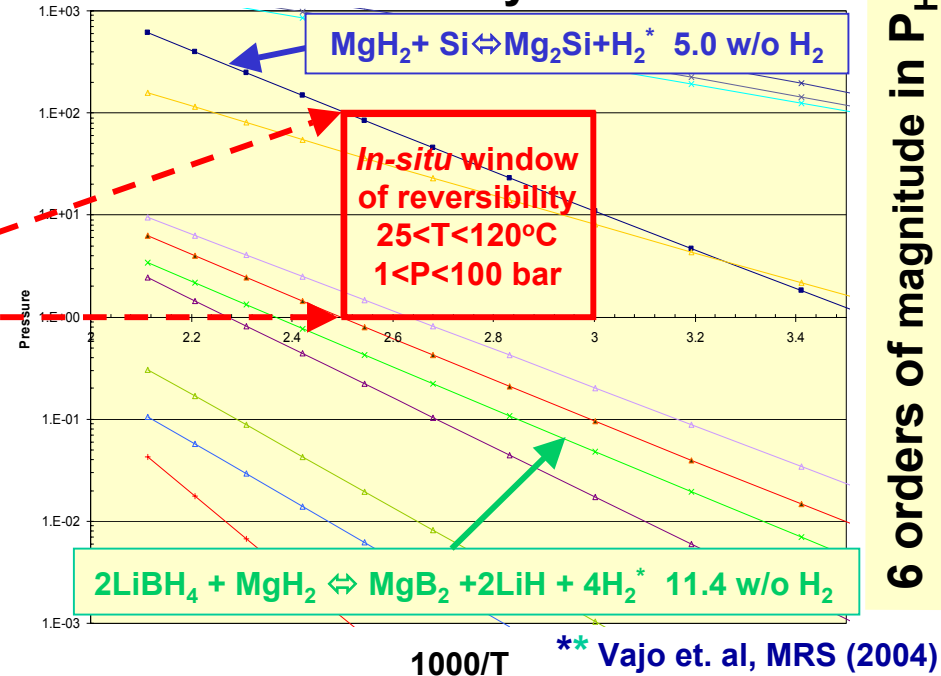
# Accomplishments

## New Hydrogen Storage Opportunities

### Complete Range of Systems



### Near Reversible Systems

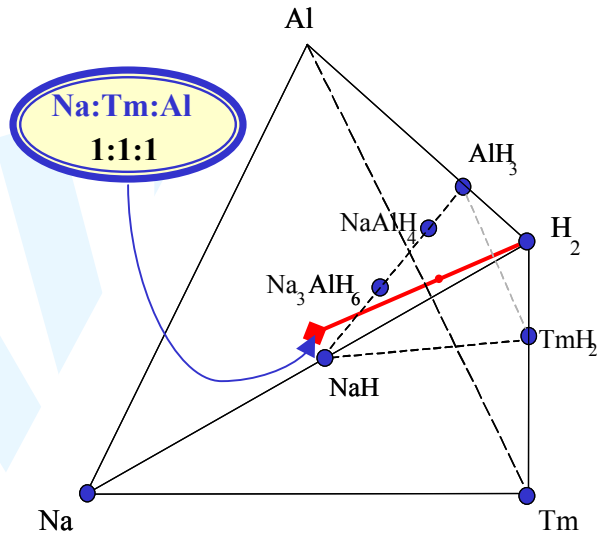


- All in-situ rechargeable systems have  $\Delta H_f \approx 40 \text{ kJ/mole H}_2$ .
- $\Delta H_f \approx 0 \text{ kJ/mole H}_2$  reactions can only be achieved at  $\sim 10^6 \text{ bar}$ .
- This results from  $\Delta S_f$  for  $\text{MH}_x$  approximately constant.

Thermodynamic assessments of *in-situ* reversible hydrogen storage reactions.

# Accomplishments

## Solid State Processing (SSP) System Surveys

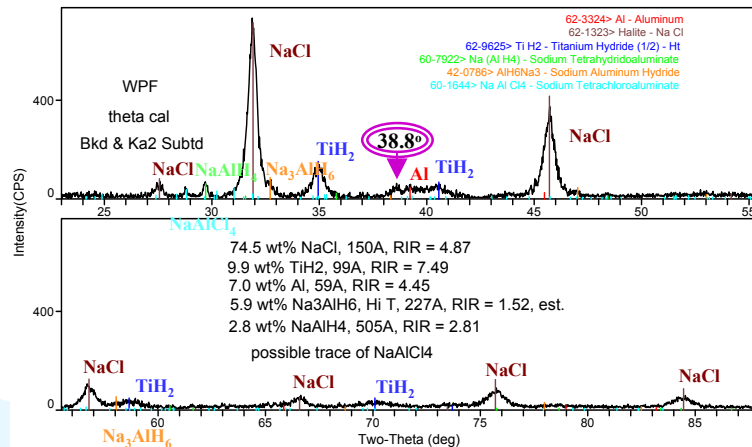


### Am/Ae/Tm

Na:Ti:Al  
Na:Li:Al  
Na:Mg:Al  
Na:Ti:Li:Al  
Na:Ti:Mg:Al  
Na:Li:Mg:Al  
Li:Mg:Al

### Processing

- Hand Mix  $\Rightarrow$  XRD
- SPEX Mill 3 hr.  $\Rightarrow$  XRD
- 200barH<sub>2</sub>/60°C/20 hr  $\Rightarrow$  XRD
- 200barH<sub>2</sub>/80°C/20 hr  $\Rightarrow$  XRD
- 200barH<sub>2</sub>/100°C/20 hr  $\Rightarrow$  XRD
- 200barH<sub>2</sub>/120°C/20 hr  $\Rightarrow$  XRD



### Analysis

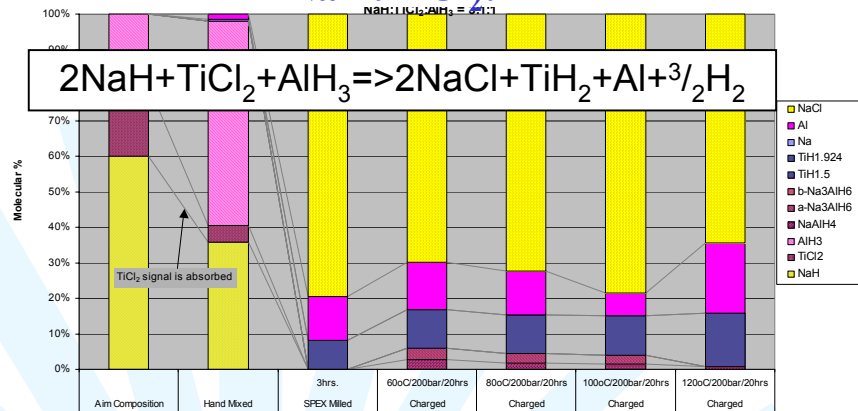
Semi-quantitative analysis using:  
**MDI Corp. Jade 7.0**  
utilizing data bases:  
**ICDD/PDF-2 Release 2002**  
**ICSD Release 2004/2.**

High throughput SSP screening of 7 quaternary/quinary systems completed.

# Accomplishments

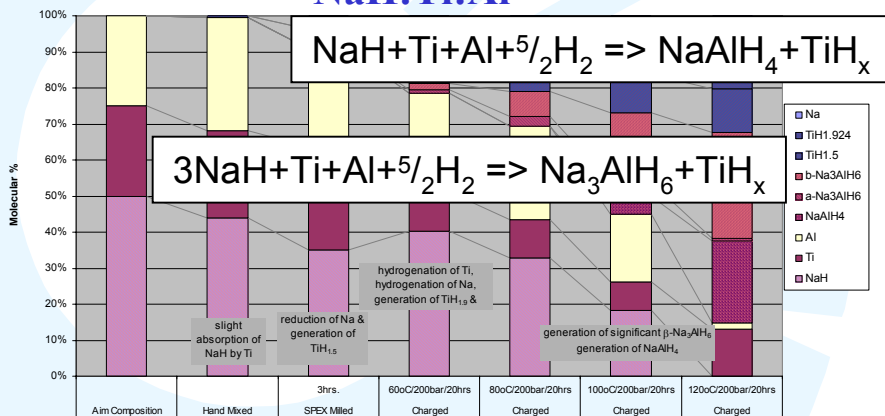
## Development of SSP NaH:TiH<sub>2</sub>:AlH<sub>3</sub> Method

NaH:TiCl<sub>2</sub>:Al



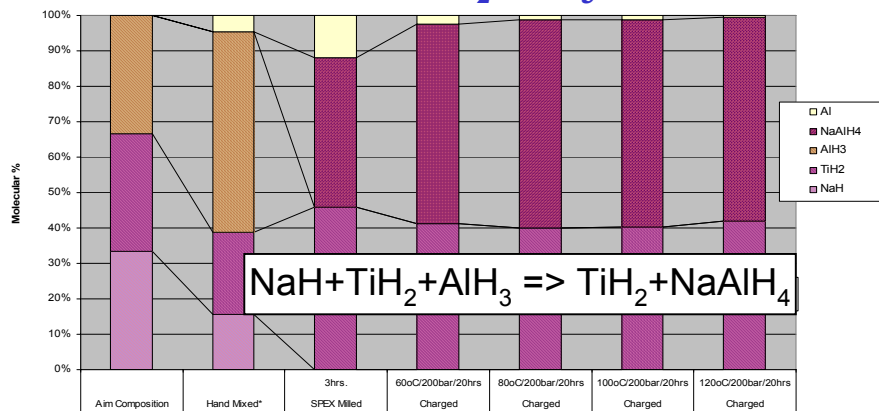
Cations introduced via chloride additions led to far too much MCl<sub>x</sub> to be effective.

NaH:Ti:Al



Primary metal additions were only an effective method of synthesizing Na<sub>x</sub>AlH<sub>y</sub> at temperatures > 100°C.

NaH:TiH<sub>2</sub>:AlH<sub>3</sub>



The most effective method was to add cations as hydride species. This method readily produced NaAlH<sub>4</sub> upon SPEX milling.

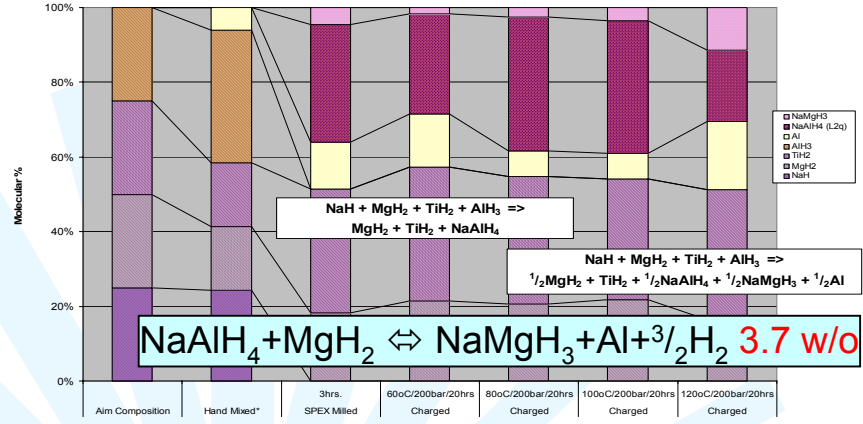
No previously unidentified phases found in the Na-Li-Ti-Al-H systems.



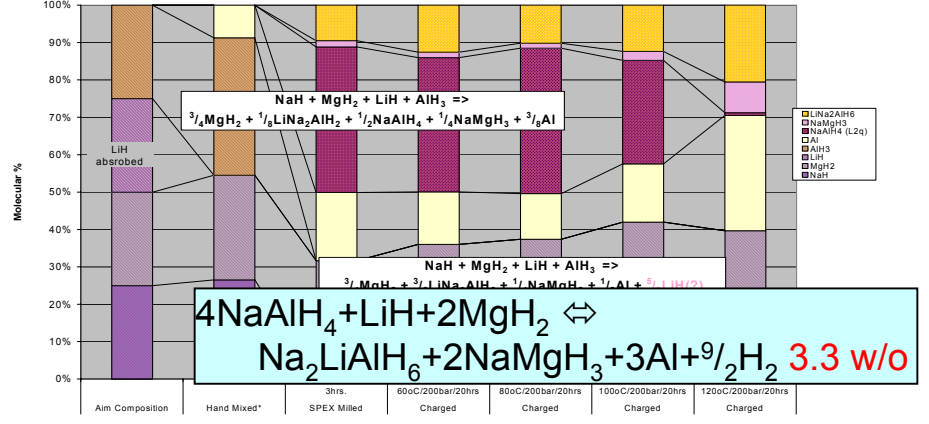
# Accomplishments

## SSP NaH-LiH:MgH<sub>2</sub>:TiH<sub>2</sub>:AlH<sub>3</sub> System Survey

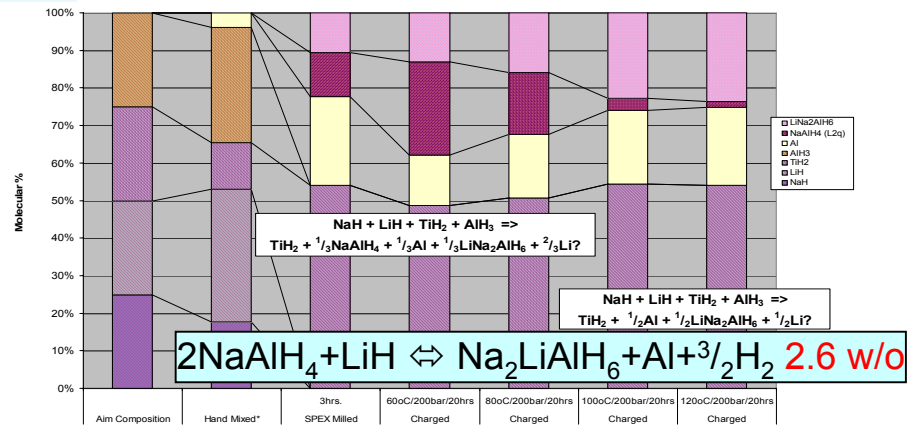
### NaH:MgH<sub>2</sub>:TiH<sub>2</sub>:AlH<sub>3</sub>



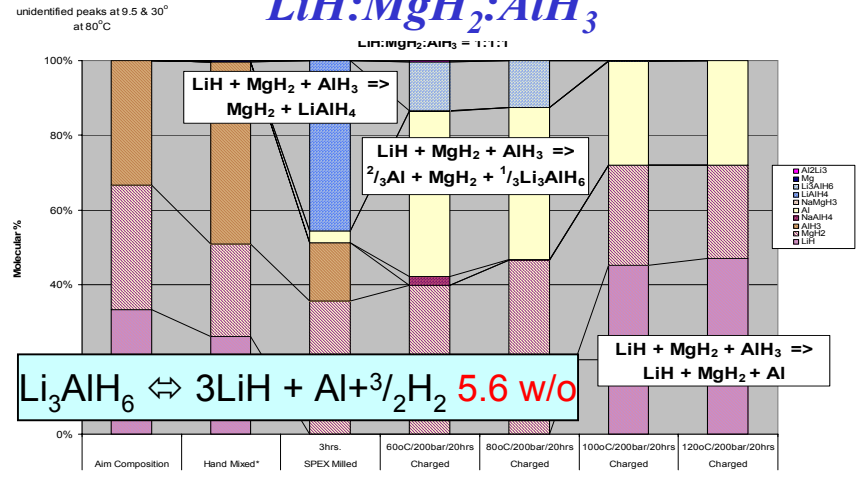
### NaH:MgH<sub>2</sub>:LiH:AlH<sub>3</sub>



### NaH:TiH<sub>2</sub>:LiH:AlH<sub>3</sub>



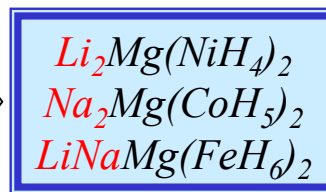
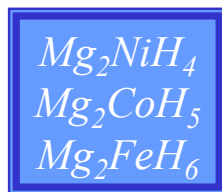
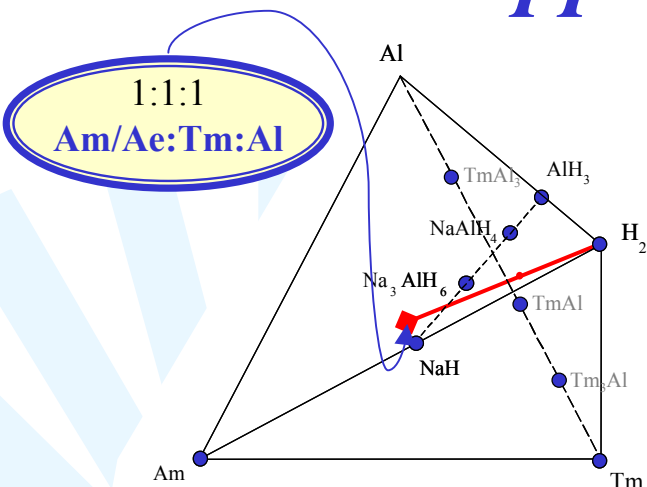
### LiH:MgH<sub>2</sub>:AlH<sub>3</sub>



Numerous mixed compound systems identified having H<sub>2</sub> capacities ranging from 2.6-5.6 w/o, and which are rechargeable ≤ 200 bar at T < 120°C.

# Accomplishments

## SSP 2005 Approach Going Forward

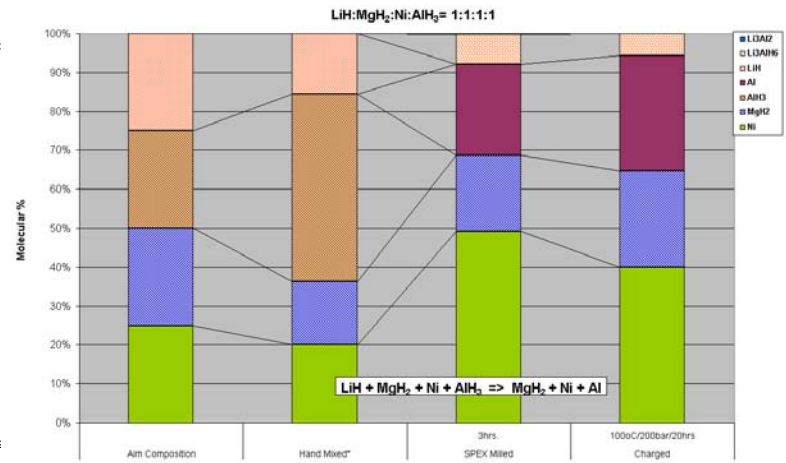
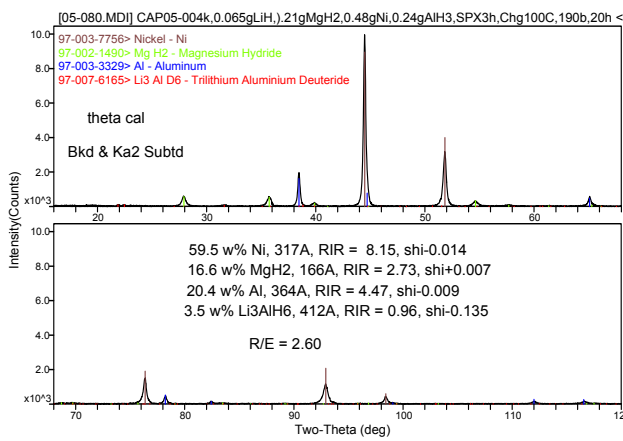


Ak/Ae/Tm

**Li:Ni:Al**  
**Na:Ni:Al**  
**Mg:Ni:Al**  
**Li:Mg:Ni:Al**  
**Na:Mg:Ni:Al**  
**Li:Co:Al**

**Na:Co:Al**  
**Mg:Co:Al**  
**Na:Mg:Co:Al**  
**Li:Fe:Al**  
**Na:Fe:Al**  
**Mg:Fe:Al**

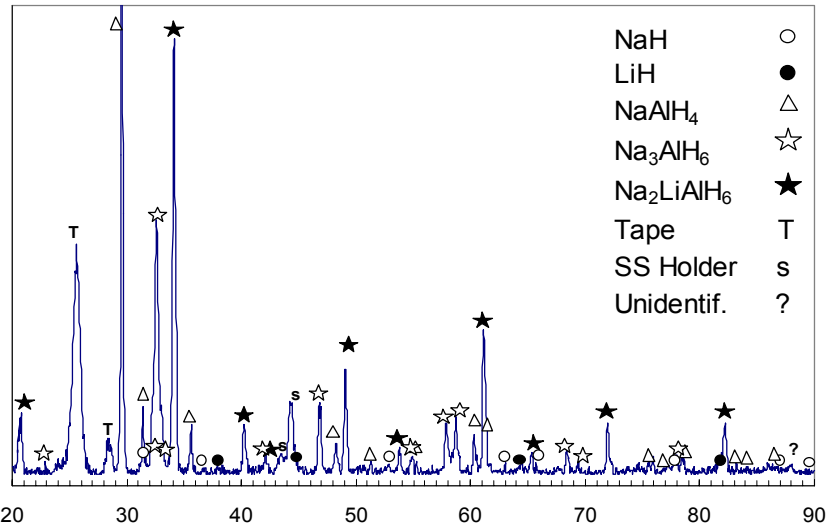
**CY '04:**  
 Hand Mix, Ball Mill  
 60, 80, 100 & 120°C  
 /200bar/20 hrs  
**CY '05:**  
 Hand Mix, Ball Mill  
 100°C/200bar/20 hrs



- Moving on to transition metal substituted systems.
- Maximize compositional ranges covered by using fewer thermal treatments.

# Accomplishments

## Molten State Processing (MSP) Proof of Concept



### Processing Conditions

190°C, 200 bar, 15 min. dwell time, agitated

### Range of Processing Conditions

RT-600°C

200 bar

8 hr dwell time

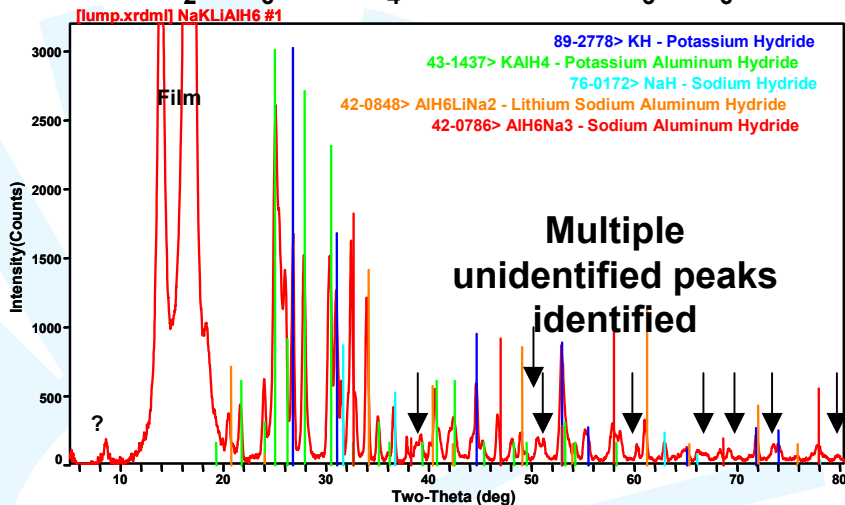
Quiescent or agitated

1 liter ~600g capacity

**Demonstrated MSP advantages: Solvent- and anion-free processing produces high yields of clean complex hydrides. One liter pressure vessel scaleable to meet system demonstration requirements.**

# Accomplishments

## MSP Compositional System Surveys

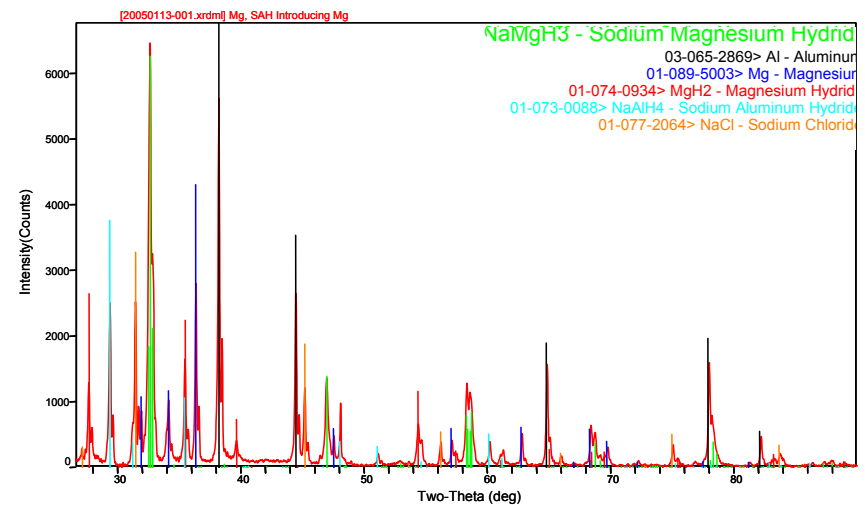


### Processing Conditions

190°C, 200 bar, 15 min. dwell time, agitated

Four quaternary/quinary composition systems investigated to date:

- Na-Li-Al-H
- Na-Ti-Al-H
- Na-K-Li-Al-H
- Na-Mg-Al-H



### Processing Conditions

190°C, 200 bar, 15 min. dwell time, agitated

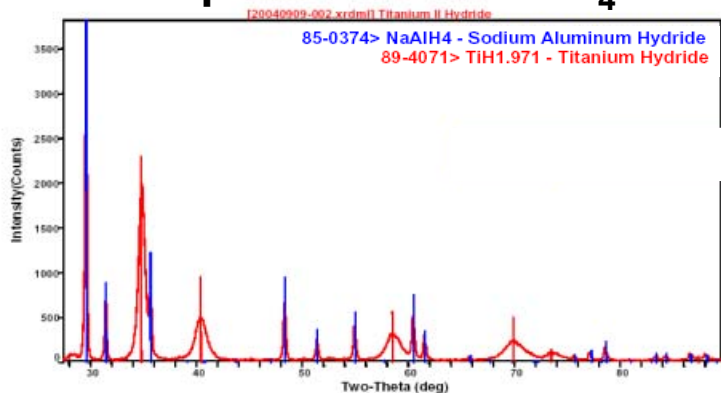
Multiple unidentified peaks observed in Na:Li:K:Al:H system provided evidence for formation of new compounds.

# Accomplishments

## MSP Produced Highly Active $\text{NaAlH}_4$

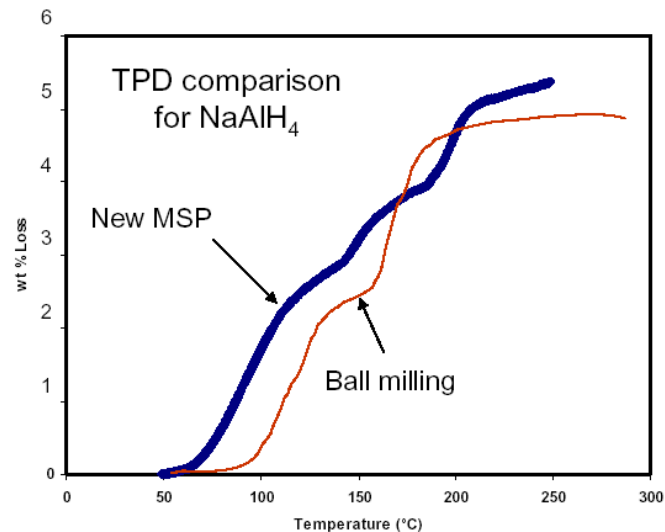
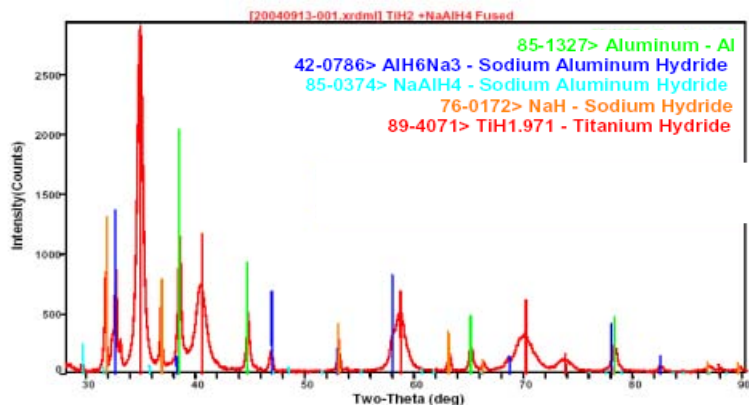
Before Fusion

Solid-state processed  $\text{NaAlH}_4 + 4\% \text{TiH}_2$



After Fusion

At 200 bar, 190°C, 15 min.



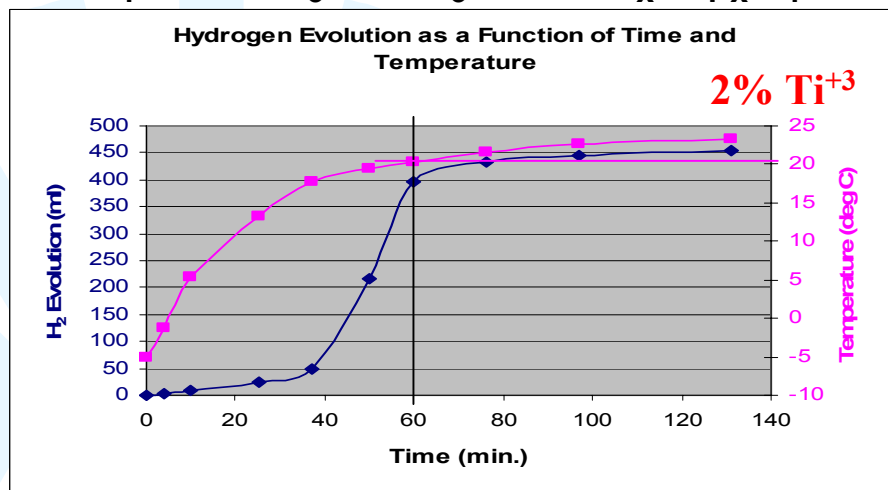
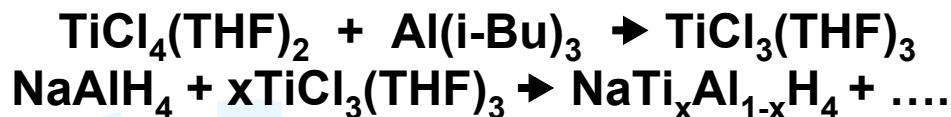
TPD discharge experiments showed MSP hydrides to be more active than conventionally ball milled hydrides. This material is being kinetically examined for possible use in CCHSS#2.

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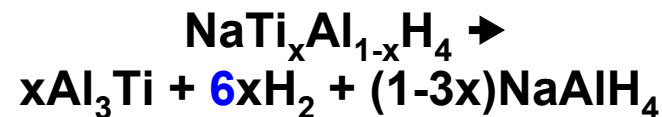
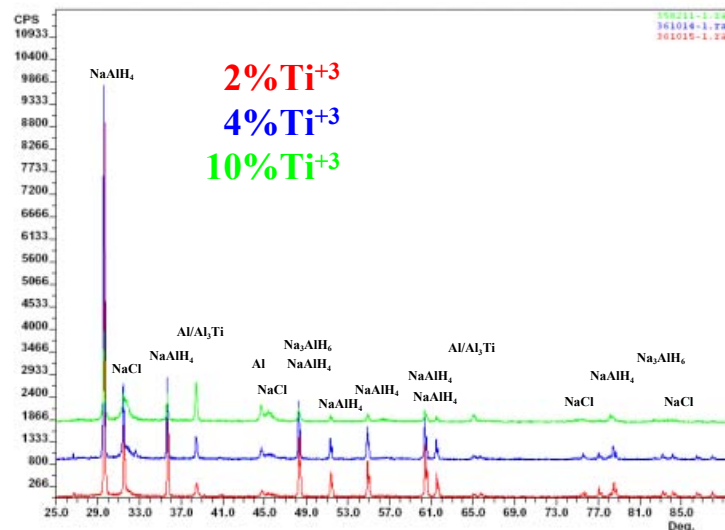
# Accomplishments

## Solution Based Processing (SBP) Ti/Na Alanates



- Complete solution doping reaction at 25°C.
- Disproportionation to Al<sub>3</sub>Ti.
- New ordered phases observed in related systems.

**Demonstrated SBP synthesis route to homogeneous Ti<sup>3+</sup> doped alanates. This material is being kinetically examined for possible use in CCHSS#2.**



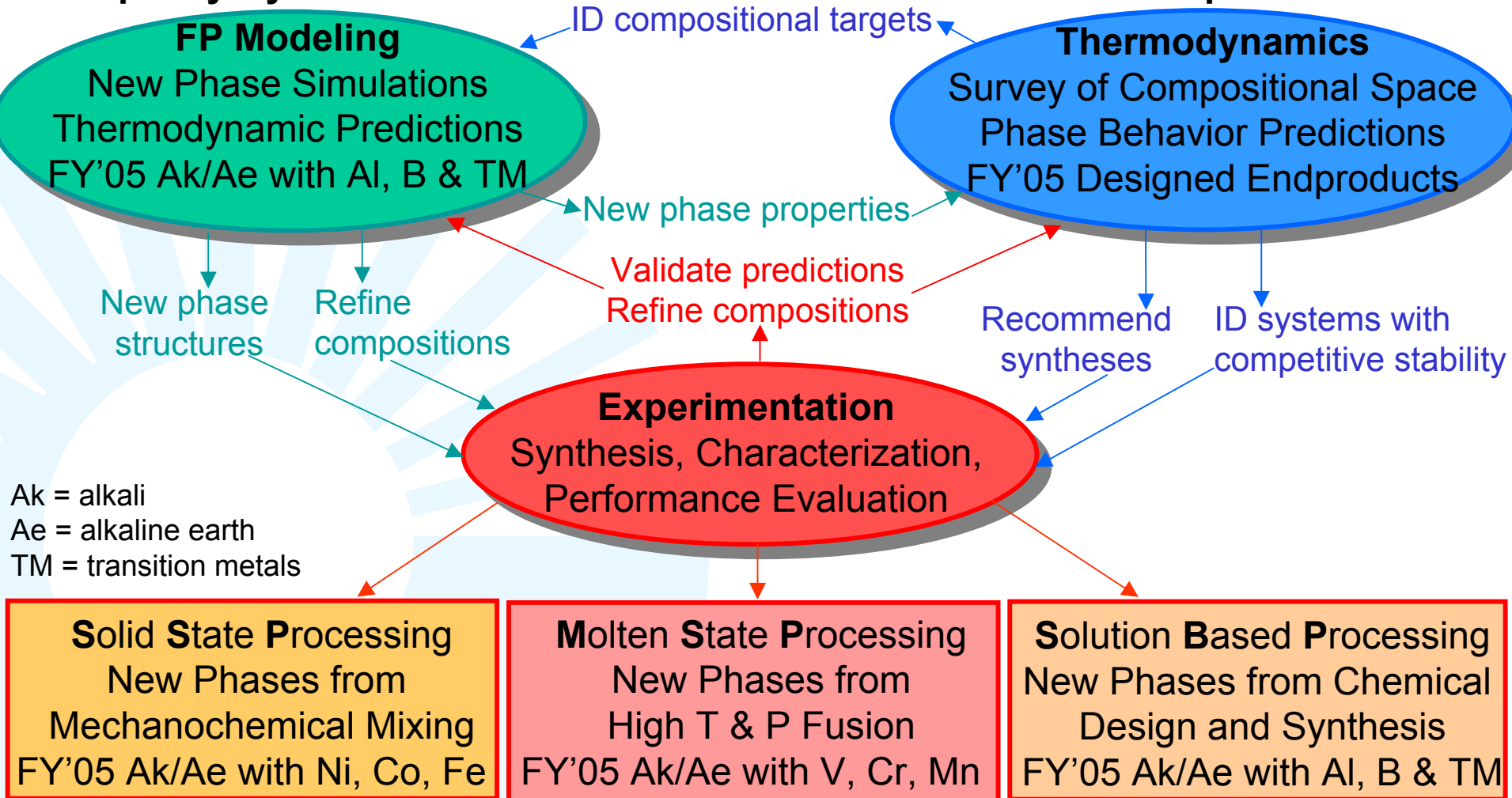
Mole ratio Ti:Al	2:100	4:100	10:100	33:100
Mole ratio H <sub>2</sub> :Ti	7.7	6.7	6.4	5.7

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# Future Work

Discovery of High H Capacity Hydrides ← **Parallel Search Strategies** → Discovery of High H Coupled Reactions



Ak = alkali  
Ae = alkaline earth  
TM = transition metals

**FY'05 Deploy integrated methods to search and discover high capacity systems.**  
**FY'06 Refine new system compositions. Catalyze improved kinetic performance.**

# *Responses to Previous Year Reviewers' Comments*

- **Comment**

“Consider broadening to include non-alanate materials?”

*By adding other complexing elements such as B, Ga ... vastly increases the scope of investigation, thus limiting empirical investigations into all possible combinations. Additions of these elements will be investigated atomistically and empirically where modeling indicates high hydrogen capacity materials are stable.*

- **Comment**

“DOE should consider how this project relates to or coordinates with the Sandia Metal Hydride Center of Excellence?”

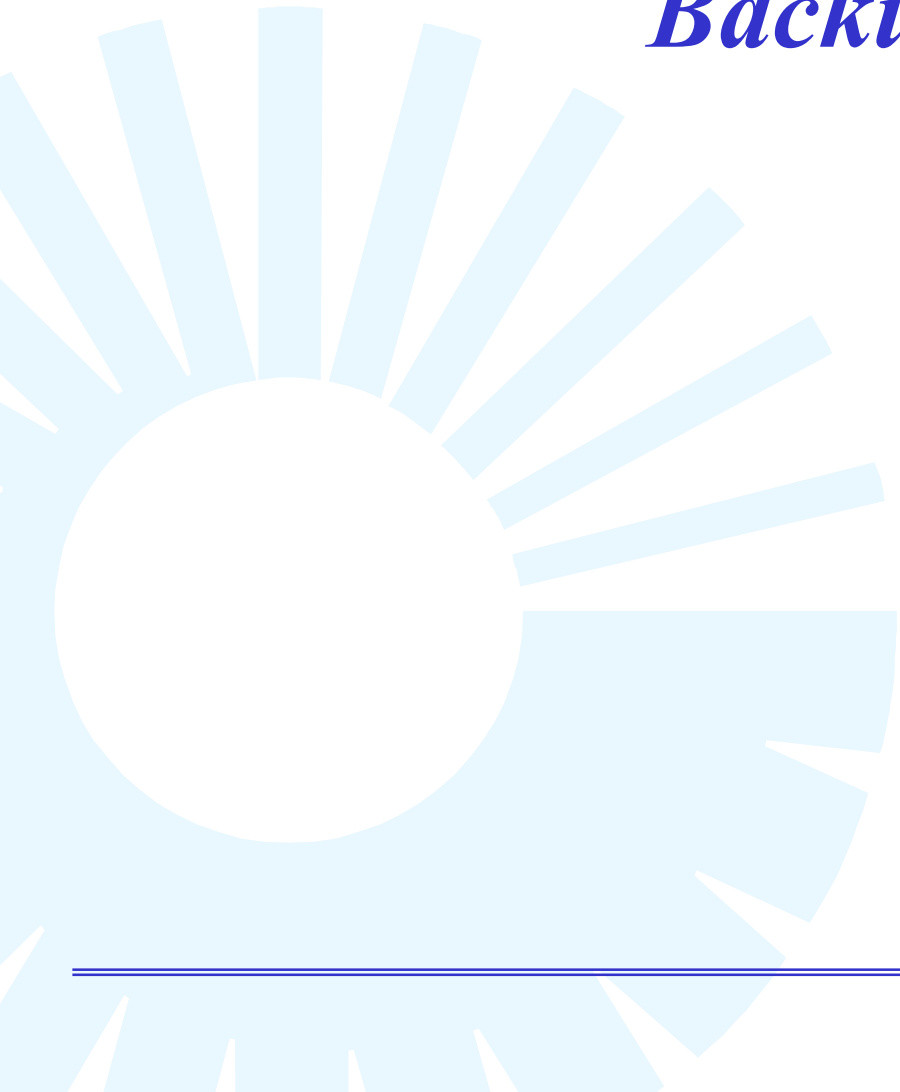
*UTRC has always maintained a high degree of communication with SNL and many of its CoE partners through DoE sponsored meetings, IEA meetings, and laboratory visits. This communication will continue.*

- **Comment**

- “Need validation that the modeling is predicting properties correctly.”
- “Need to insure that the modeling efforts are not independent of experiment.”

*As shown in the progress to date, modeling and empirical results have shown very good agreement. We have a very high confidence level in modeling predictions when phonon approach is incorporated. The modeling & empirical efforts are designed to be interdependent with each other, and are closely coordinated with monthly meetings used to exchange data, ideas, and concepts.*

# *Backup Slides*



# *Publications*

O. M. Løvvik, S. M. Opalka, H. W. Brinks, and B. C. Hauback, "Crystal structure and thermodynamic stability of the lithium alanates  $\text{LiAlH}_4$  and  $\text{Li}_3\text{AlH}_6$ ," Phys. Rev. B 69 134117-134125 (2004).

H.W. Brinks, B.C. Hauback, C.M. Jensen, and R. Zidan, "Synthesis and crystal structure of  $\text{Na}_2\text{LiAlD}_6$ ," J. Alloys Compd. 392(1-2) 27-30 (2005).

O. M. Lovvik and S. M. Opalka, "First-principles calculations of Ti-enhanced  $\text{NaAlH}_4$ ," Phys. Rev. B 71 054103-1-10 (2005).

O. M. Lovvik, O. Swang, and S. M. Opalka, "Modeling alkali alanates for hydrogen storage by density-functional band-structure calculations" submitted 4/05 J. Mater. Res.

C. Qiu, S. M. Opalka, G. B. Olson, and D. L. Anton, "The Na-H System: from First Principles Calculations to Thermodynamic Modeling," submitted 4/05 Phys. Rev. B. Two related papers on the Na-Al-H and Na-Ti-Al-H system currently in preparation.

# *Presentations*

O. M. Løvvik and S. M. Opalka, "First-principles calculations of Ti-enhanced  $\text{NaAlH}_4$ ." International Symposium of Metal Hydrogen Systems (MH2004), Cracow, Poland, September 10, 2004.

R. Zidan, "Development and Characterization of Complex Hydrides," Invited Speaker, ASM Material Solution Conference, Columbus, OH, Oct. 18-21, 2004.

R. Zidan, "Hydrogen Storage R&D Key Issues for the Hydrogen Economy," and "Solid-State Hydrogen Storage Systems," Hydrogen Economy Workshop, Invited Speaker as Representative for the Department of Energy, Cairo, Egypt, January 31 – February 2, 2005.

C. Qiu, S. M. Opalka, D. L. Anton, and G. B. Olson, "Thermodynamic Modeling of Sodium Alanates," Materials Science & Technology 2005, to be held in Pittsburgh, PA, on September 25-28, 2005.

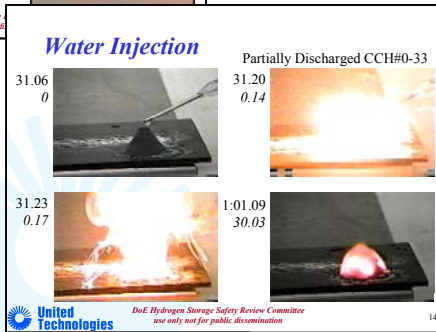
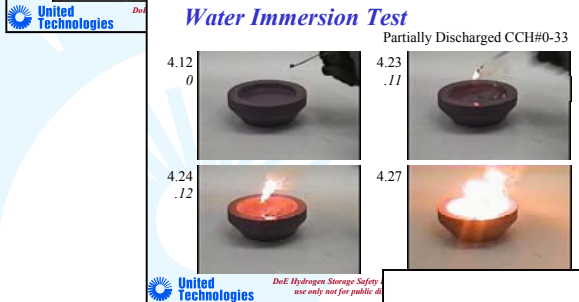
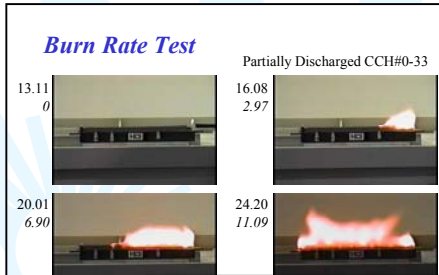
S. M. Opalka, O. M. Lovvik, H. W. Brinks, B. C. Hauback, and D. L. Anton, "Combined Experimental-Theoretical Investigations of the Na-Li-Al-H System," Materials Science & Technology 2005, to be held in Pittsburgh, PA, on September 25-28, 2005.

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**Multiple collaborations foster  $\text{H}_2$  storage research progress and communication.**

# Safety

## Risk Identification



Explosion risks quantitatively assessed



**Dust Explosion Testing**

*\*Dust explosion: class St-3, Highly Explosive when finely divided and dispersed.*

	Test Materials		Reference Materials	
	NaAlH <sub>4</sub>	NaH+Al	Pitt. Seam Coal Dust	Lycopodium Spores
P <sub>max</sub> bar-g	11.9	8.9	7.3	7.4
R <sub>max</sub> bar/s	3202	1200	426	511
K <sub>st</sub> bar-m/s	969	326	124	139
Dust Class	St-3	St-3	St-1	St-1
MEC g/m <sup>3</sup>	140	90	65	30
MIE mJ	<7	<7	110	17
T <sub>c</sub> °C	137.5	137.5	584	430

P<sub>max</sub> = maximum explosion pressure, R<sub>max</sub> = pressure rise rate, K<sub>st</sub> = maximum rate of pressure rise, MEC = minimum explosion concentration, MIE = minimum spark ignition energy, T<sub>c</sub> = maximum dust cloud ignition temperature

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Fire risk quantitatively assessed

**Appendix V- UTRC Risk Assessment Form**

Date	Room Number	Participants
5/4/04	S145H	Tom Ververis, Xia Tang, Ron Brown, Jodi Vecchiarrelli

No	Process, Task or Step	Potential hazard	Controls in Place	Likelihood Occurrence	Potential Impact	Risk Rank	Controls Required To reduce risk further/Name/Date
1	Mixing Powder Media Preparation	Fire, Explosion	All work is done in glovebox filled with Nitrogen Containers inside glove box sealed Gloves inspected every day Nitrogen pressure checked every day Moisture and O2 sensor in glovebox Positive pressure maintained in glove box	2	3	6 Med	
2	Hydrogen Storage Running Test	Failure of High Pressure Systems Fire, Explosion	Restricted use Risk assessments Local rules and procedures Pressure rated components Pressure relief valves Automatic controllers; Redundant valves Detailed Procedures; Employee training Critical valve Maintenance Remote gas line shutoff and purge if loss of power or ventilation All test stands in hoods All equipment leak tested (H2 sniffer) Flash arrestor Moisture filters	2	3	6 Med	Lower Pressure
3	Hydrogen Storage, Running Test	High Temp, Oil Bath, Burns, Oil spill	Warning sign "Hot Oil" Secondary containment Redesigned Jack stand gnd in place Located in hood.	2	2	4 Low	
4	Vacuum System (Hydrogen), Running Test	Explosion	Special Hydrogen Vac. Pumps Sparkless	2	3	6 Med	
5	Working in glovebox	Ergonomic pain	Limited time in glovebox to 45 minutes max. Set up to avoid awkward reaching	2	2	4 Low	
6	Lifting, transporting samples	Ergonomics	Training, procedures Weight kept to < 30 pounds	2	2	4 Low	

Comprehensive risk assessment performed on all major operations quantitatively describing both impact and probability of occurrence.

# Safety

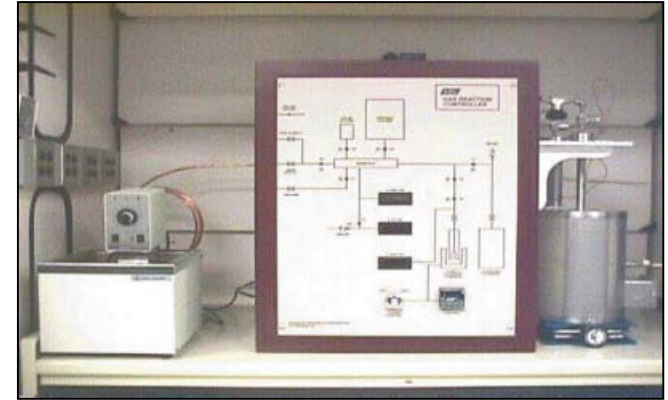
## Risk Mitigation



**Material handled under inert gas**



**Incoming material stored in fire cabinet**



**Materials tested in commercial equipment installed in a glove box**



**Media stored under inert gas**

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**All risks reduced to low impact or negligible probability.**