Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods

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Project ID # STP23

A Honeywell Company

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Overview

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Timeline

- Start date: 5/1/2004
- End date: 6/30/2008
- % Complete: 90

Budget

- Total project funding
  - DOE: $2,400,000
  - UOP: $3,010,618
  - Ford: $ 75,000
- FY07 DOE: $471,193
- FY08 DOE: $400,000

Barriers

- Barriers addressed (DOE-2010)
  - Useable H_2 Density
    - 2.0 kWh/kg & 1.5 kWh/L
  - H_2 Delivery Temperature Range
    - -40 to 85˚C
  - Cycle Life
    - 1000 Cycles

Partners

- Hawaii Hydrogen Carriers
- UCLA
- Ford
- Striatus

Objectives

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• **Overall**	• **Discovery of a complex metal hydride through Molecular Modeling and Combinatorial Methods which will enable a hydrogen storage system that meets DOE 2010 goals** • **Deliverables:** ◆ Optimized material ◆ Sample for independent testing at SWRI ◆ Documentation
• **2004/2005**	• **Validation and Demonstration of VHTS (Molecular Modeling)** • **Validation and Demonstration of Medium Throughput Combinatorial Tools** • **Downselect from Na, Li, Mg/AlH_4**
• **2005/2006**	• **Demonstration of High Throughput Combinatorial Tools** • **Identification of New Materials Approaching DOE Targets**
• **2006/2008**	• **Search for New Hydrogen Storage Materials using High Throughput Combinatorial Tools** • **Identification and Characterization of New Materials Meeting DOE Targets**

High Throughput vs. Traditional Approach

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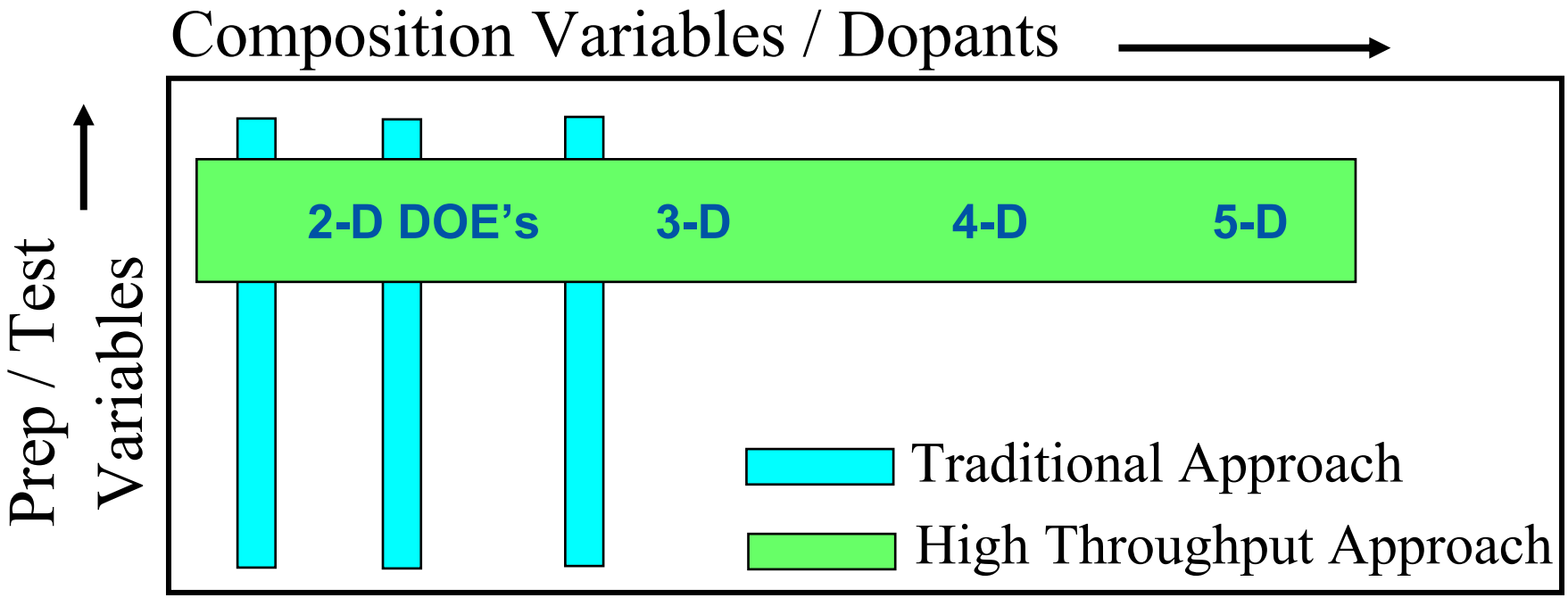
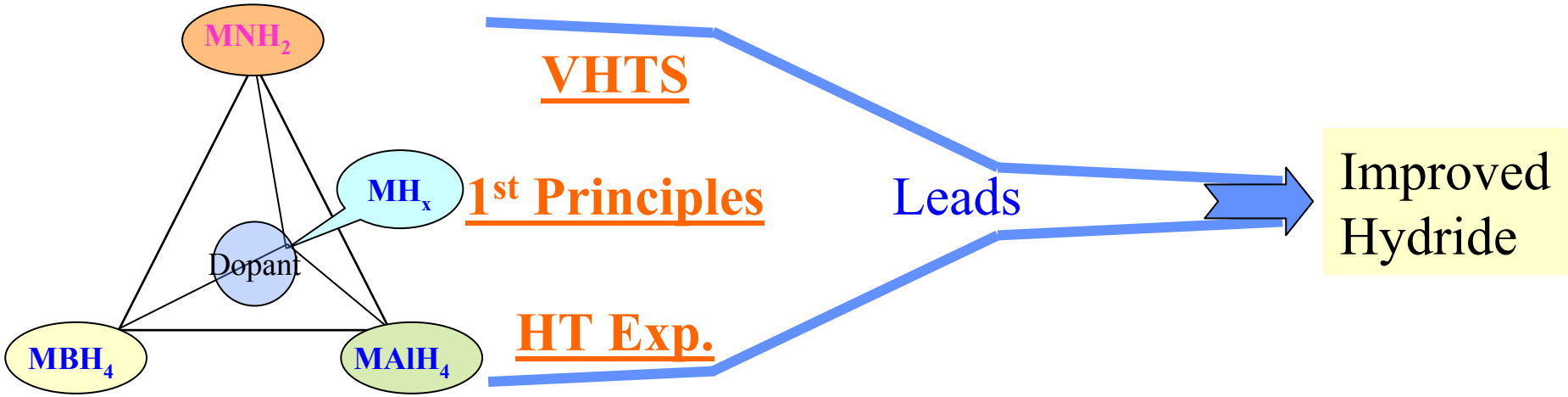


- **Total Hydride/Dopant/Process-Variable space is too large even for our Combi methods to fully explore, given time & resources.**
- **HT Tools are more difficult, costlier to develop/modify than Single-Sample tools, this limits Combi "Prep/Test" Space.**
  - **Synthesis methods, measurement conditions**
  - ***Selected milling approach based on state-of-the-art at project start***
- **Even with these limitations a vast phase space is available for searching by Combi methods.**
- **Goal of Combi is to find leads, additional measurements & characterization can be done using traditional methods.**

Overall Project Approach



- **Modeling**
  - Virtual High Throughput Screening, ~1000 compositions/month
  - DFT to predict new materials with favorable thermodynamics, refine leads
- **Combi Synthesis & Screening**
  - High Throughput (up to 48x)
  - Discrete, scalable sample preparation using ball-milling or solution-phase
- **Follow up on Leads:**
  - Characterization & modeling for increased understanding
  - Optimization, scale-up & multi-cycle testing

Technical Accomplishments 2007-2008

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Since last Peer Review:

- Project ran from 5/1/2004 to 4/30/2007
- Project was extended
  - UOP only
  - Bring High Throughput Synthesis System on-line
- Funds for extension came through 1Q 2008
- Currently working with vendor to remedy problems with HT Synthesis System
- Will proceed with chemistry once HT Synthesis System is fixed
- High Throughput Hydrogen Storage Capacity Assay Modified

High Throughput Testing Capability

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- **Capability:**
  - Comparison of Medium Throughput (MT) and High Throughput (HT) systems:

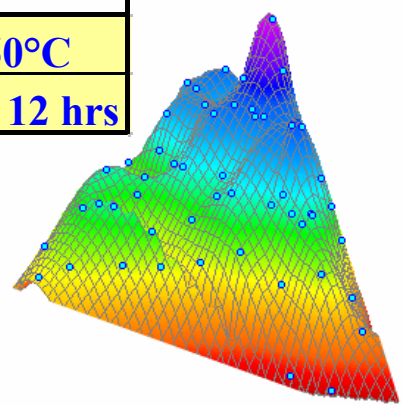
	MT Assay	HT Assay
No of Rx:	8	48
Max T:	220°C	350°C
Max P:	87 bar	120 bar
Desorption P:	Variable	~1 bar abs.

- **Test Protocol:**
  - Perform multiple cycles of temperature programmed desorption + rehydriding:

Std. Cond.	MT Assay	HT Assay
Desorption	To 220°C	Multiple T: 100-350°C
Rehydriding	125°C, 87 bar, 12 hours	100-125°C, 120 bar, 12 hrs

  - Second cycle represents reversible wt-%H

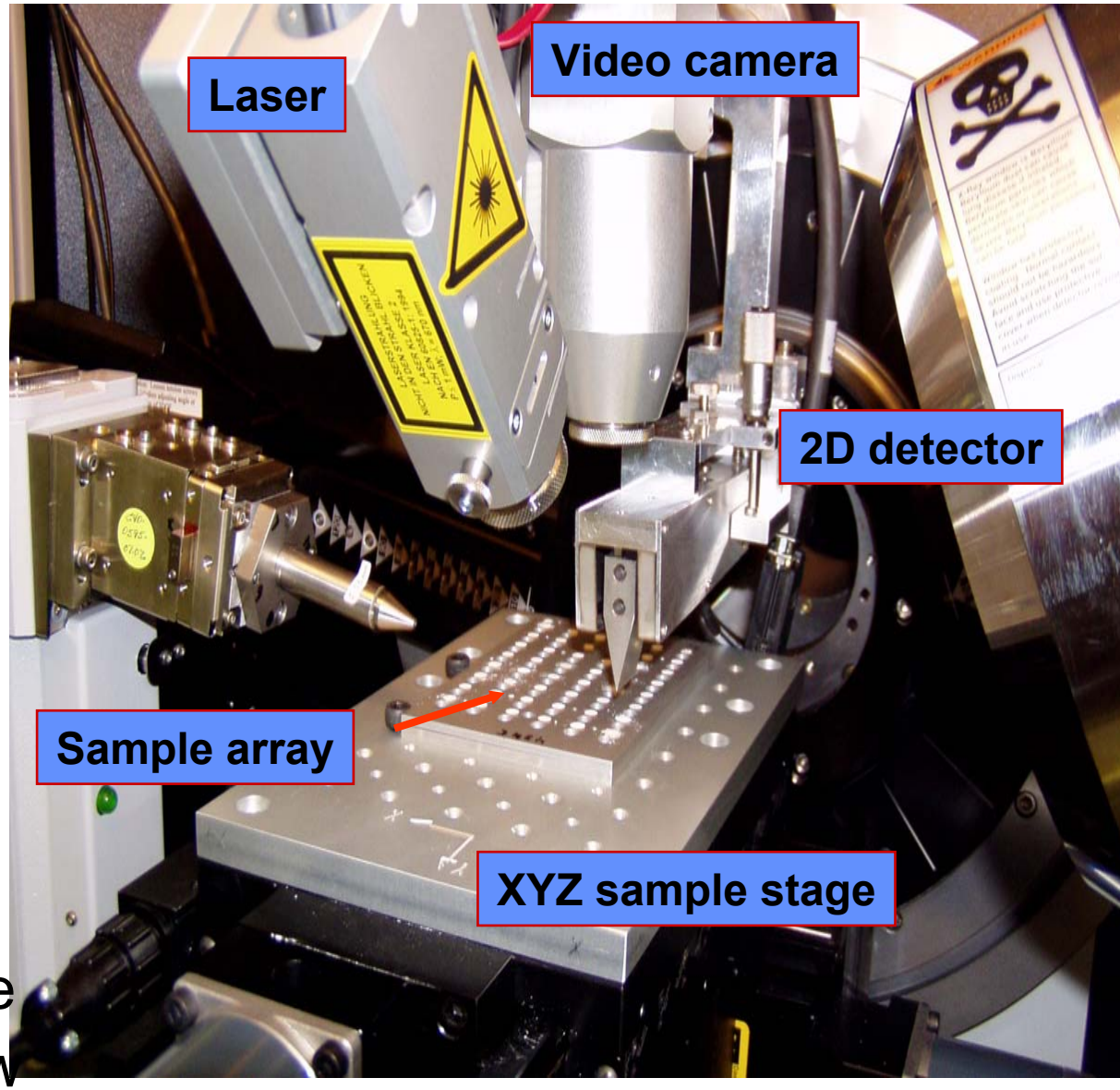
- **Status:**
  - **Both MT and HT Systems are operational**



Phase Diagram
measured by HT Assay

Combinatorial (High Throughput) XRD Assay

- Automated XYZ sample stage
- Area Detector
- Each xrd collected in 60 sec
- 48 samples/plate
- Follow structural transformations associated with H_2 absorption/desorption
- Selected structural transformations encountered over in the project presented below



Following Absorption/Desorption Chemistry

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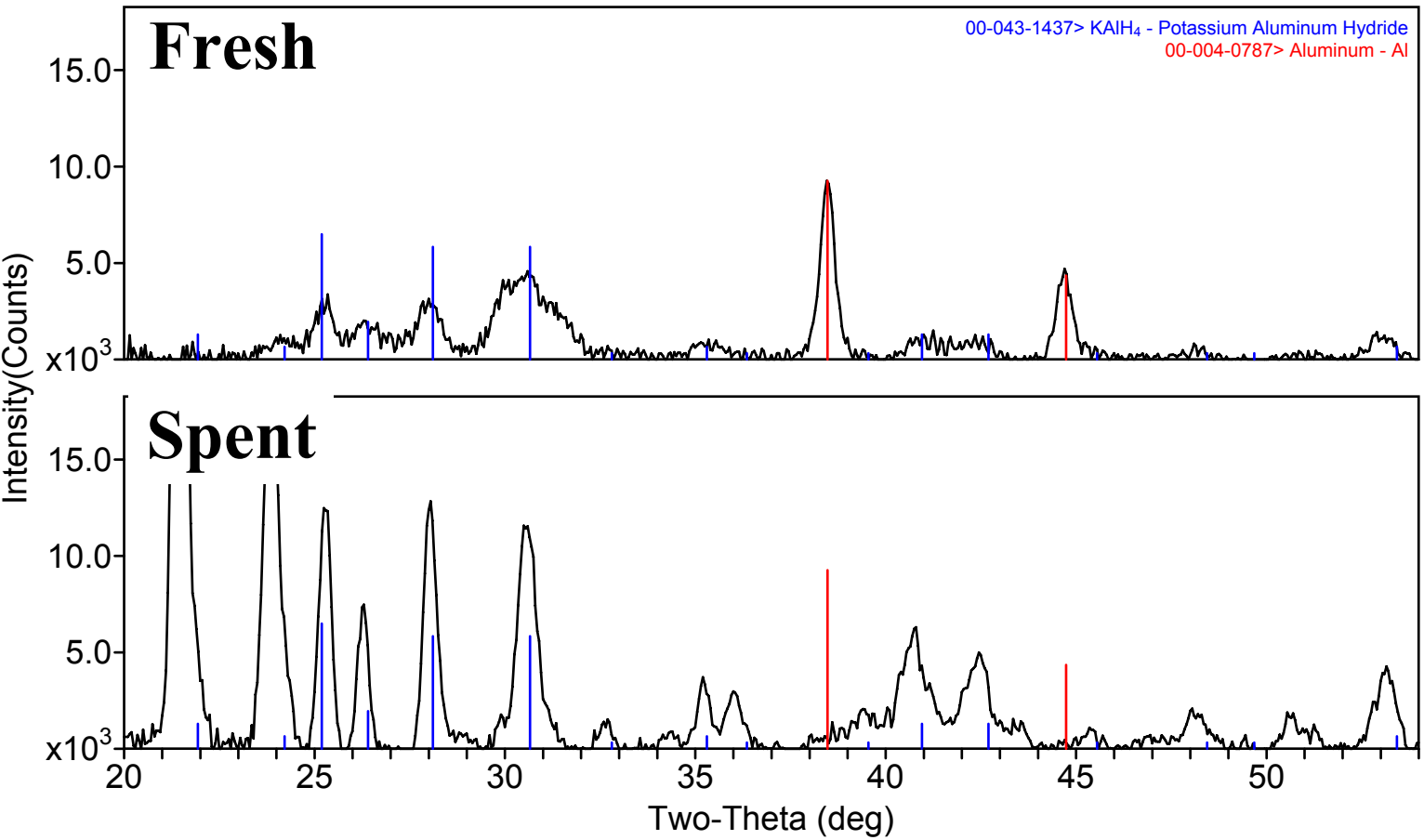
System: KH + AlH_3/0.02 $Ti(OiPr)_4$

- After milling: Al + $KAlH_4$, some alane decomposition
- Spent: $KAlH_4$; hydriding steps led to stable $KAlH_4$ that did not desorb hydrogen under test conditions



Medium Throughput (MT) Assay

$\underline{H_2 \text{ Capacity}}$

Cycle #1

0.50 wt. %

Cycle #2

0.18 wt. %

Following Absorption/Desorption Chemistry

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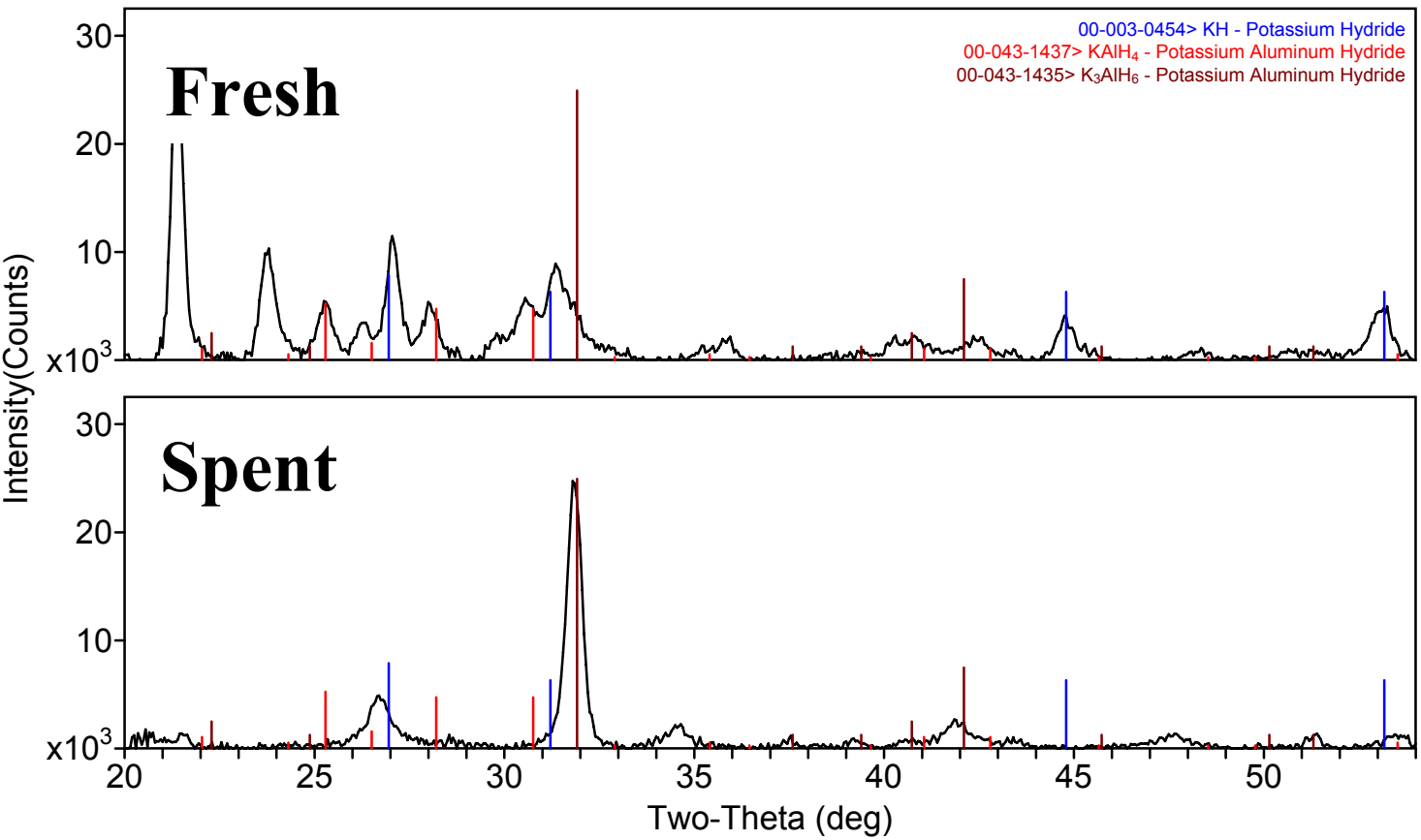
System: $LiAlH_4$ + 2 KH/0.02 $Ti(OiPr)_4$

- After Milling: KH + $KAlH_4$ (ion-exchange)
- Spent: K_3AlH_6 (conproportionation, stable, little desorption)



MT Assay

H_2 Capacity

Cycle #1

0.28 wt. %

Cycle #2

0.12 wt. %

Following Absorption/Desorption Chemistry

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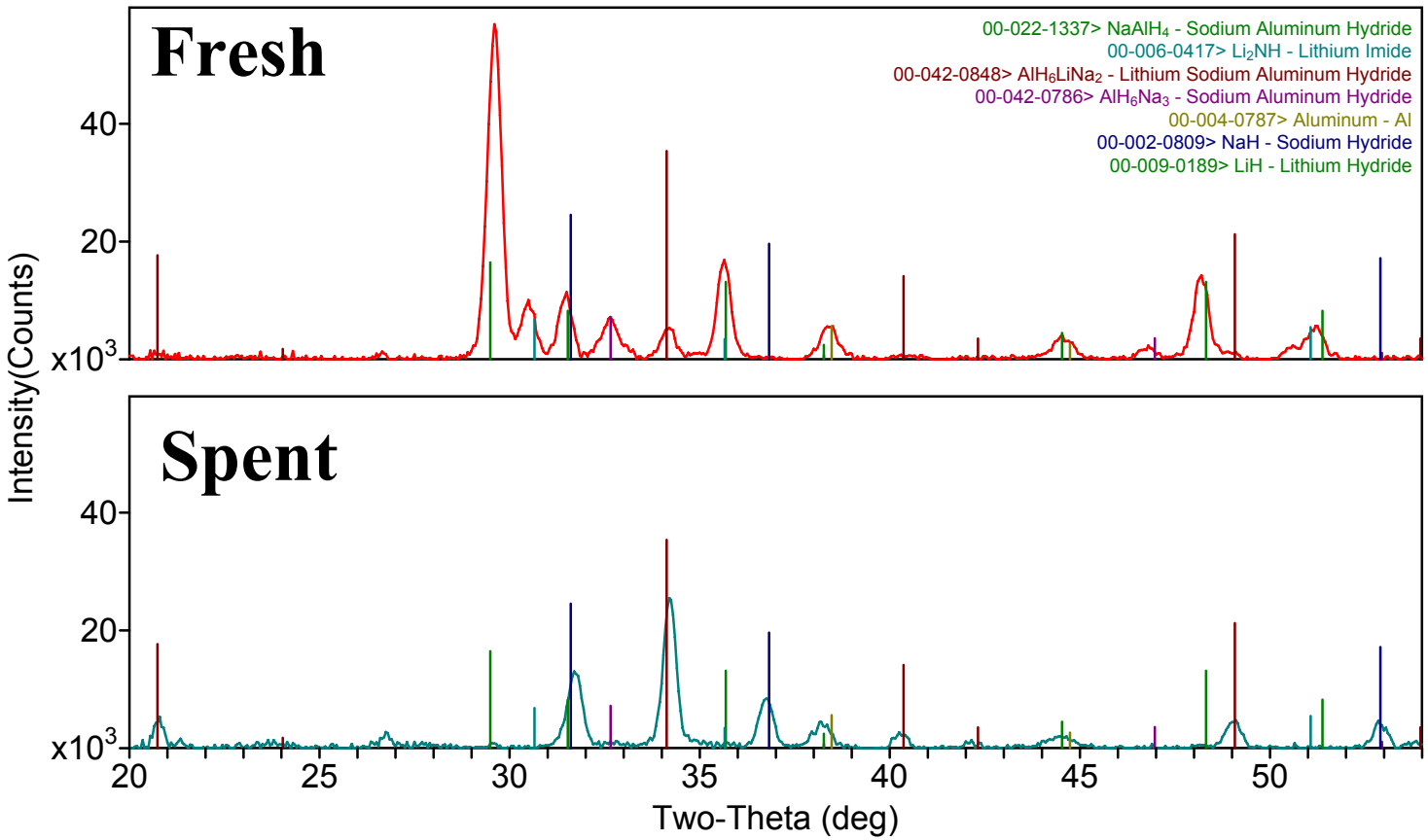
System: 2 $NaAlH_4$ + $LiNH_2$/0.04 $Ti(OiPr)_4$

- After Milling: $NaAlH_4$ + Li_2NH + Na_3AlH_6 + Al + $LiNa_2AlH_6$ (H_2 evolution, ion-exchange during milling)
- Spent: $LiNa_2AlH_6$ + NaH + LiH + $NaAlH_4$; $LiNa_2AlH_6$ main reversible phase



MT Assay

H_2 Capacity

Cycle #1

2.14 wt. %

Cycle #2

1.01 wt. %

Following Absorption/Desorption Chemistry

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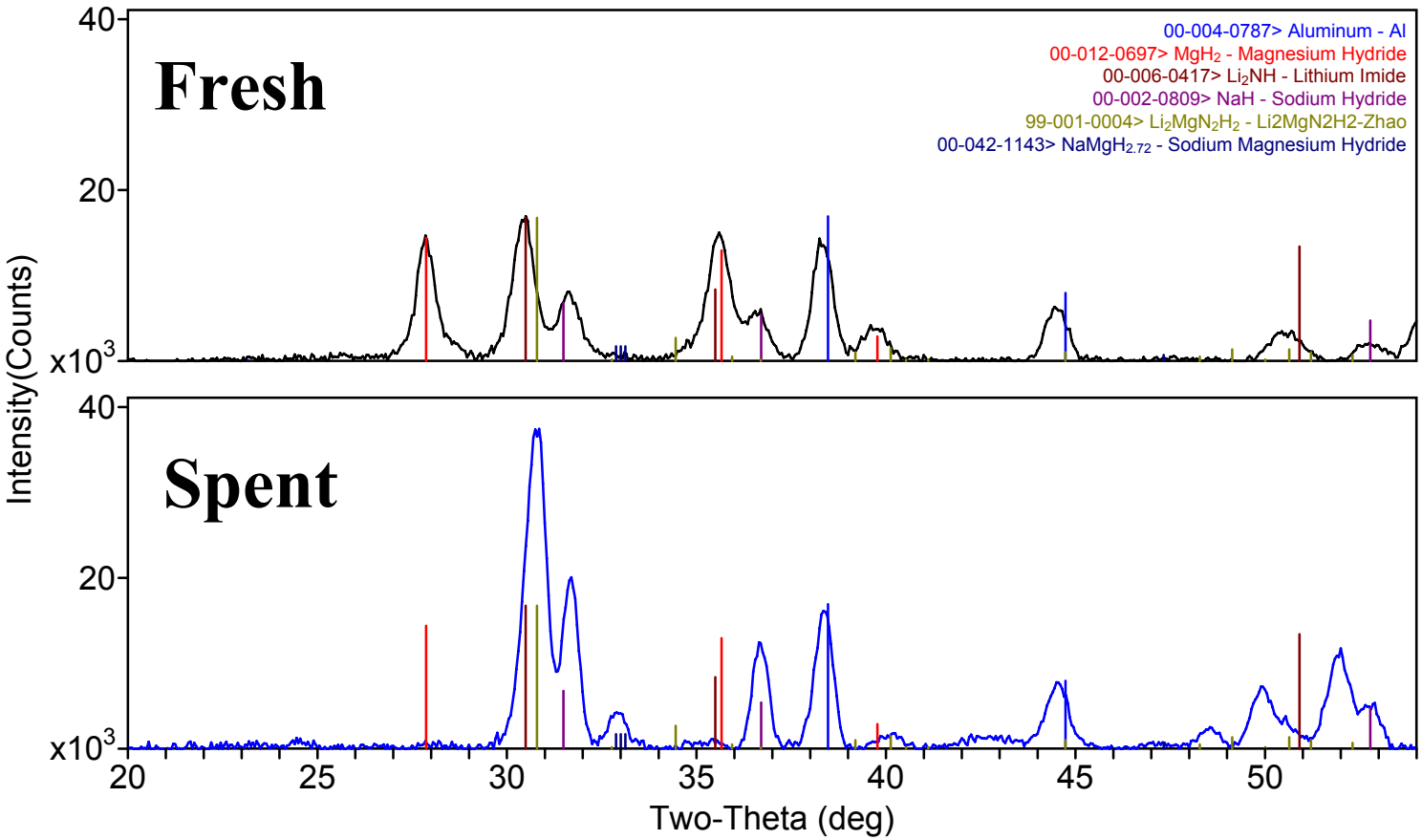
System: 4 $LiNH_2$ + 2.2 MgH_2 + NaH + Al/0.02 $Ti(OiPr)_4$

- After Milling: Li_2NH + MgH_2 + Al + NaH (H_2 evolution)
- Spent: $Li_2Mg(NH)_2$ + NaH + Al + $NaMgH_3$; reversible system is combination of $NaAlH_4$ and $LiNH_2$ – MgH_2 systems



MT Assay

H_2 Capacity

Cycle #1

3.45 wt. %

Cycle #2

1.45 wt. %

Following Absorption/Desorption Chemistry

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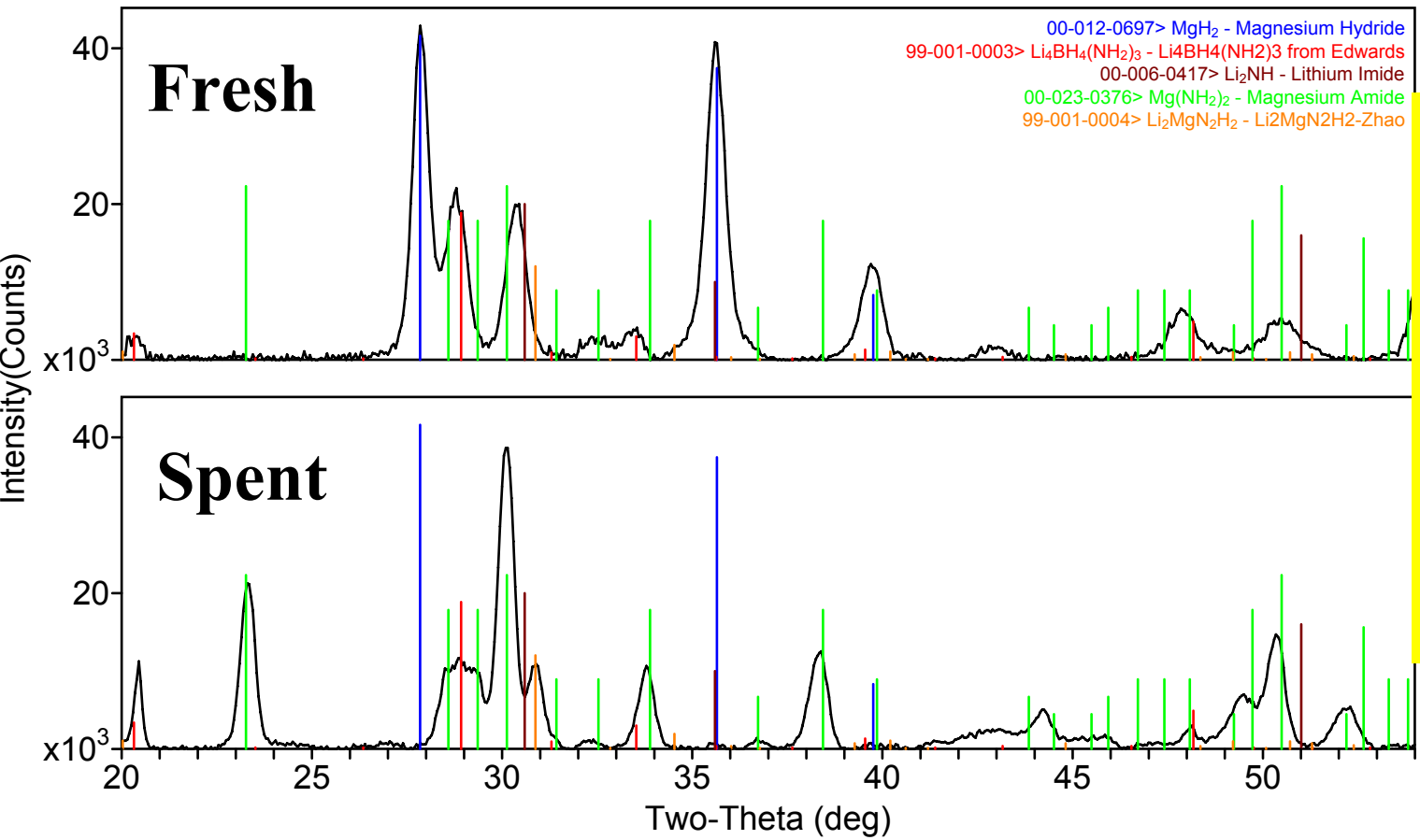
System: 5 $LiNH_2$+ $LiBH_4$+ 2.2 MgH_2

- After Milling: MgH_2 + $Li_4(NH_2)_3BH_4$ + Li_2NH (formation of mixed Li amide-borohydride, enhances reversibility)
- Spent: $Mg(NH_2)_2$ + $Li_4(NH_2)_3BH_4$ + $Li_2Mg(NH)_2$



MT Assay

H_2 Capacity

Cycle #1

3.89 wt. %

Cycle #2

3.41 wt. %

Following Absorption/Desorption Chemistry

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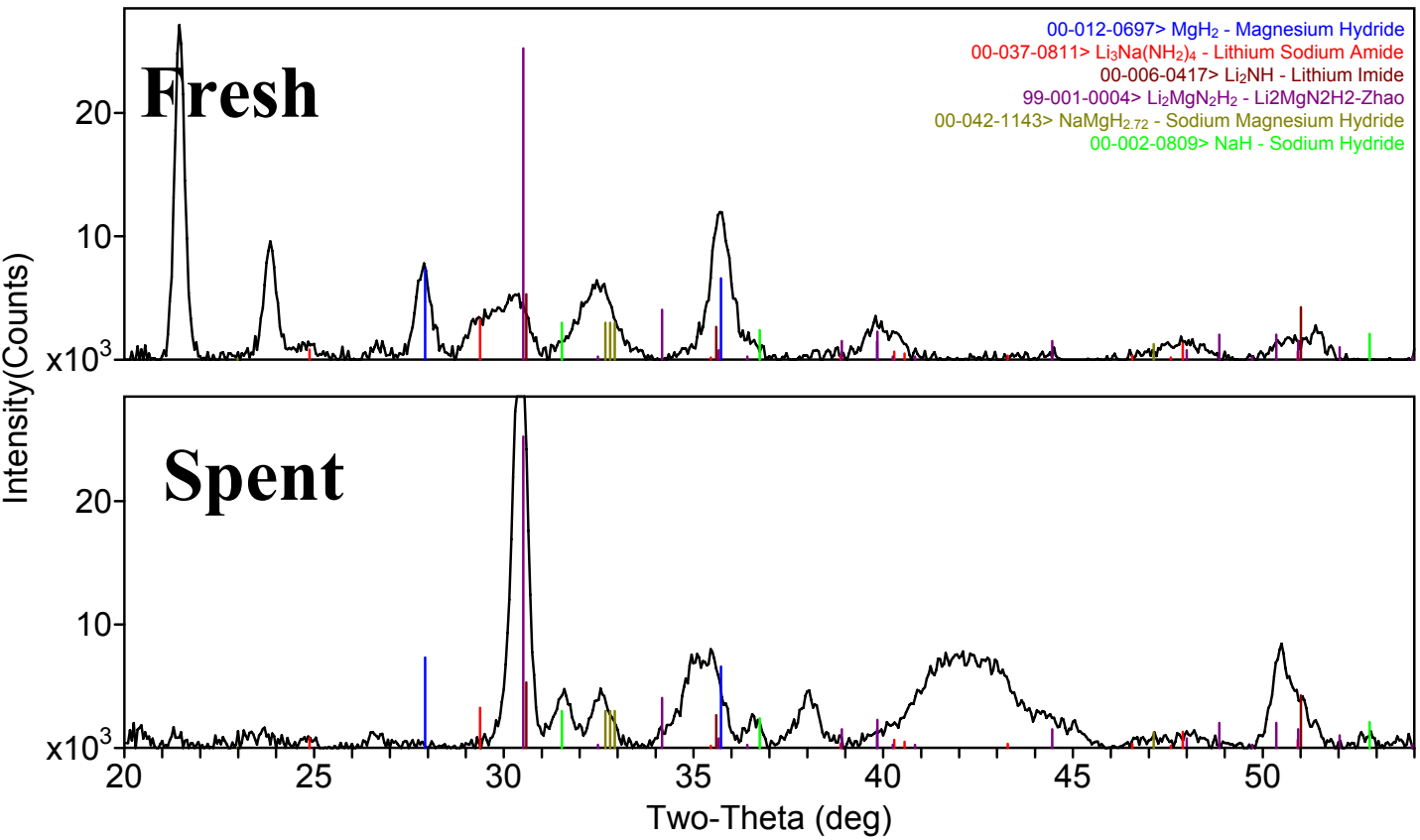
System: 0.75 $LiNH_2$ + 0.25 $NaNH_2$ + 0.25 MgH_2 /0.02 $Ti(OiPr)_4$

- **After Milling: MgH_2 + $Li_3Na(NH_2)_4$ + $Li_2NH/LiNH_2$ (formation of mixed Li-Na amide)**
- **Spent: $Li_2Mg(NH)_2$ + $Li_2NH/LiNH_2$ + NaH + $NaMgH_3$ (reversible $LiNH_2$-MgH_2 system competes with irreversible $NaMgH_3$)**



MT Assay

H_2 Capacity

Cycle #1

1.09 wt. %

Cycle #2

0.28 wt. %

Following Absorption/Desorption Chemistry

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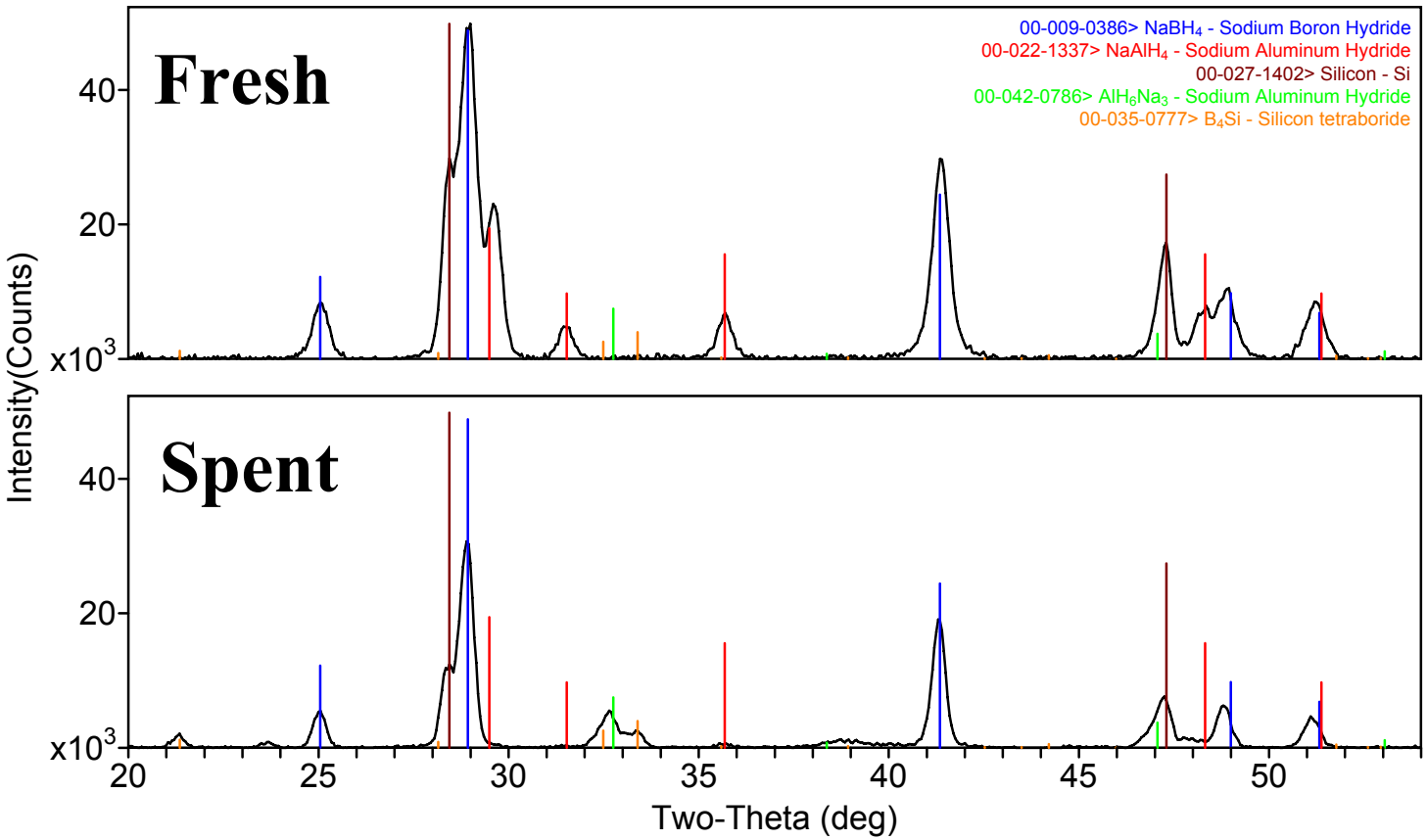
System: 4 $NaBH_4$ + $NaAlH_4$ + Si/0.1 $Ti(OiPr)_4$

- After Milling: $NaBH_4$ + Si + $NaAlH_4$
- Spent: $NaBH_4$ + Si + Na_3AlH_6 + B_4Si (Activation of Si at low temperature to form B_4Si)



MT Assay

H_2 Capacity

Cycle #1

1.03 wt. %

Cycle #2

0.38 wt. %

HT vs. MT Synthesis of Hydrogen Storage Materials

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MT Synthesis

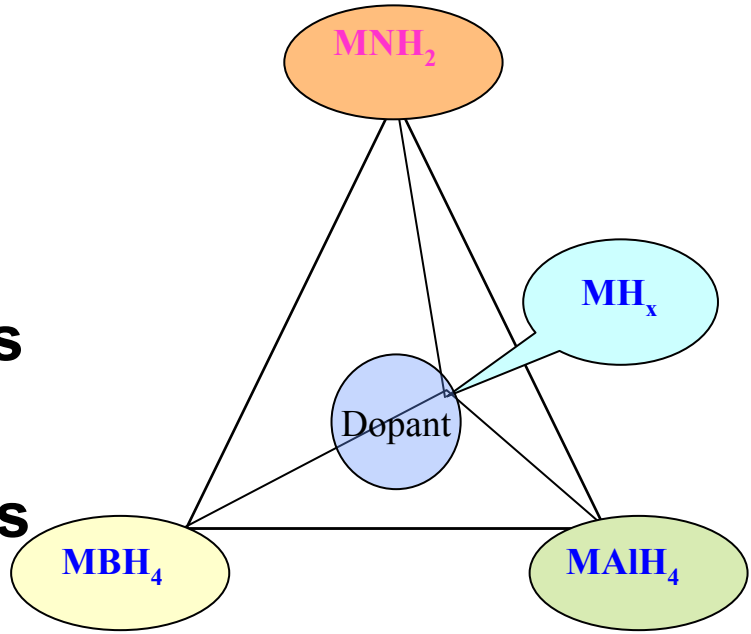
- Solid reagents in powder form are mixed by milling
- Planetary ball mill employed
- Synthesis on 1 g scale
- 45 ml tungsten carbide milling bowl, 18-10 mm tungsten carbide balls, milled at 350 rpm for 30 minutes
- Requires significant manpower

HT Synthesis

- Pre-milled powders employed
- Synthesis on 150 mg scale
- Both Solution and Solid State Chemistry
- Robotic powder and solvent delivery
- Parallel Milling of combined powders
  - 48 at a time
  - Low Energy, uses 5mm stainless steel balls
- Reproducible and accurate dosing of pre-milled powders remains an obstacle

Plans

- Employ HT Synthesis once powder dosing is operational
- Continue with Metal hydride amide–borohydride-alanate phase diagrams
- Amide-borohydride is favored because of low melting temperatures (e.g., $Li_4(NH_2)_3BH_4$)



- Micellar-type reactions which take advantage of the low melting point of Li-amide-borohydride systems
- Synthesis from solution
- Traditional solid state synthesis (milling) in the parallel HT synthesis apparatus; benchmark against traditional tools

Project Summary

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- VHTS and First Principles modeling capabilities
  - Predicted alanate mixtures do not meet DOE targets
  - Identified several potential reactions with desired energetics
- Medium Throughput Assay (8 Reactors)
  - Investigated $LiAlH_4$-$NaAlH_4$-$Mg(AlH_4)_2$/Ti phase diagram
  - Investigated rehydriding reactions with Al, alkali and alkaline earth hydrides/Ti
  - Confirmed modeling results that alanates do not meet DOE targets
  - Also applied to non-alanate studies
- High Throughput Assay (48 Reactors)
  - Measured multi-cycle capacities 1000+ samples in many phase diagrams including the components Li, Na, Mg, Al, Ti, Zr, Mn, V, Cr, Mo, Co, Ni, Cu, Zn, and some mixtures
  - Investigation of $LiNH_2$-$LiBH_4$-MgH_2 phase diagram found kinetic enhancement due to the formation of $Li_4(NH_2)_3BH_4$, which melts during desorption/absorption
- High Throughput Synthesis System
  - Scan of 15 dopants carried out on two base materials
- Mixtures of Complex Hydrides have yielded few new compounds, and those found have not met DOE targets for hydrogen storage.

Lessons Learned

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- Combinatorial approach works very well for finding optimum compositions in multinary phase diagrams
- High throughput equipment is more complex, takes longer to develop than single-sample methods
- Medium Throughput Assay (8 Reactor)
  - [+] Worked well
- High Throughput Assay (48 Reactor)
  - [+] Screened ~ 1000 experimental samples (+ refs. in every run)
  - [-] Labor intensive - high maintenance
  - [-] Sample size too small for characterization after test
- High Throughput Synthesis System
  - [+] Wide synthesis capability
  - [-] Development, shakedown
  - [-] Accurate handling of milled powders
  - [-] Sample transfer equipment

Lessons Learned, cont.

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- **Virtual High Throughput Screening**
  - [+] When models ready, very fast & covers high-dimensional space
  - [+] Even negative results are valuable (after experimental validation): give confidence to move focus elsewhere
  - [+] Not limited to known structures
  - [+] Provided insight to alanates: heats of mixing too low to yield mixtures with desired thermodynamics
  - [-] Development of new force fields takes a long time
- **First Principles Modeling**
  - [+] Provided insights into thermodynamics of $LiNH_2$ – MgH_2 – $LiBH_4$ system
  - [+] Generated several new leads with promising thermodynamics
  - [-] Experimental follow up disappointing – kinetics?
  - [-] Computationally expensive, dev. of high-throughput algorithms
  - [-] Accuracy highest for known structures
- **Modeling Needs:**
  - Ability to predict kinetics & dopant effects

The Team

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DOE Project Manager

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Syed Faheem – Synthesis
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