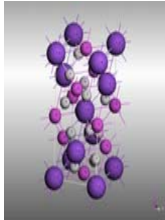


# Development and Characterization of Complex Hydrides

Molten State Processing  
in Support of UTRC Material Discovery Project



**SRNL**<sup>TM</sup>  
SAVANNAH RIVER NATIONAL LABORATORY

**We Put Science To Work**

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Savannah River National Laboratory

May 23-25, 2005

**Project ID # STP58**

# Overview

## Timeline

- 3 yr CRADA
- began May 28, 2004
- Approx. 33% complete

## Budget

- Total CRADA Funding = \$900K
  - \$450K DOE
  - \$450K UTRC & Partners
- \$110K receive in FY04
- \$150K received in FY05

## Barriers

- General Onboard H2 Storage (A-G)
- Reversible Solid-State Material Storage (M-Q)
- Target is to meet DOE 2007 and 2010 Hydrogen Storage Goals

## Partners

- United Technology Research Center (CRADA Partner)
- Institute for Energy (IFE) in Norway
- Albemarle Corp. Baton Rouge, LA

# Objective

The ultimate objective of this research is to develop a low-cost hydrogen storage material with high capacity, cyclic stability and possessing favorable thermodynamics and kinetics compatible with the DOE onboard hydrogen transportation goals.

## Specific Objectives

- Discover new complex hydride compounds  $\text{Na}_y\text{M}_{+ix}(\text{AlH}_4)_{y+ix}$  based on NaH,  $\text{AlH}_3$ , transition metal or rare earth (M) hydrides.
- Material capable of reversibly storing  $\text{H}_2 > 7.5 \text{ wt } \%$  and  $> 500$  cycles
- The overall UTRC led program will examine 3 parallel synthesis methods – SRNL will utilize its own patent pending Molten State Process.

## **Task 1 – Complex Hydride Alloying**

### **Task 1.1 - Material Synthesis and Modification**

**The SRNL molten state process (MSP) will be used to develop new hybrid alanate compounds by combining or “alloying” together different aluminum hydride compounds. Transition metal aluminum hydrides containing Ti, Zr, Mn, Fe etc. will be alloyed with alkaline and alkaline earth aluminum hydrides containing K, Na, Li, Mg, and Ca.**

**The SRNL MSP has unique operating conditions that allow these materials to interact and combine leading to a much higher probability of success over traditional ball milling and chemical processing techniques. SRNL already has the equipment, facilities and knowledge base to efficiently perform this work and has already proven the fundamental aspects and advantages of the molten state process with complex metal hydrides.**

# Approach (Cont.)

## **Task 1.2 - Material Characterization**

**Structural characterizations and physical property analyses will be employed to identify newly synthesized complex hydride phases. X-ray diffraction and differential scanning calorimetry (DSC) analyses will be the primary tools.**

## **Task 1.3 Modeling to Guide Material Synthesis**

**The theoretical modeling of structures, and phase stabilities will be coordinated with those from UTRC and compared with results obtained from characterization and spectroscopic studies.**

# High Pressure MSP System



# Material Development

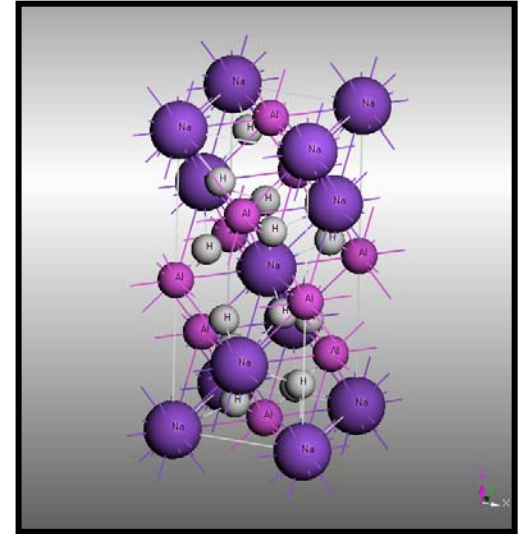
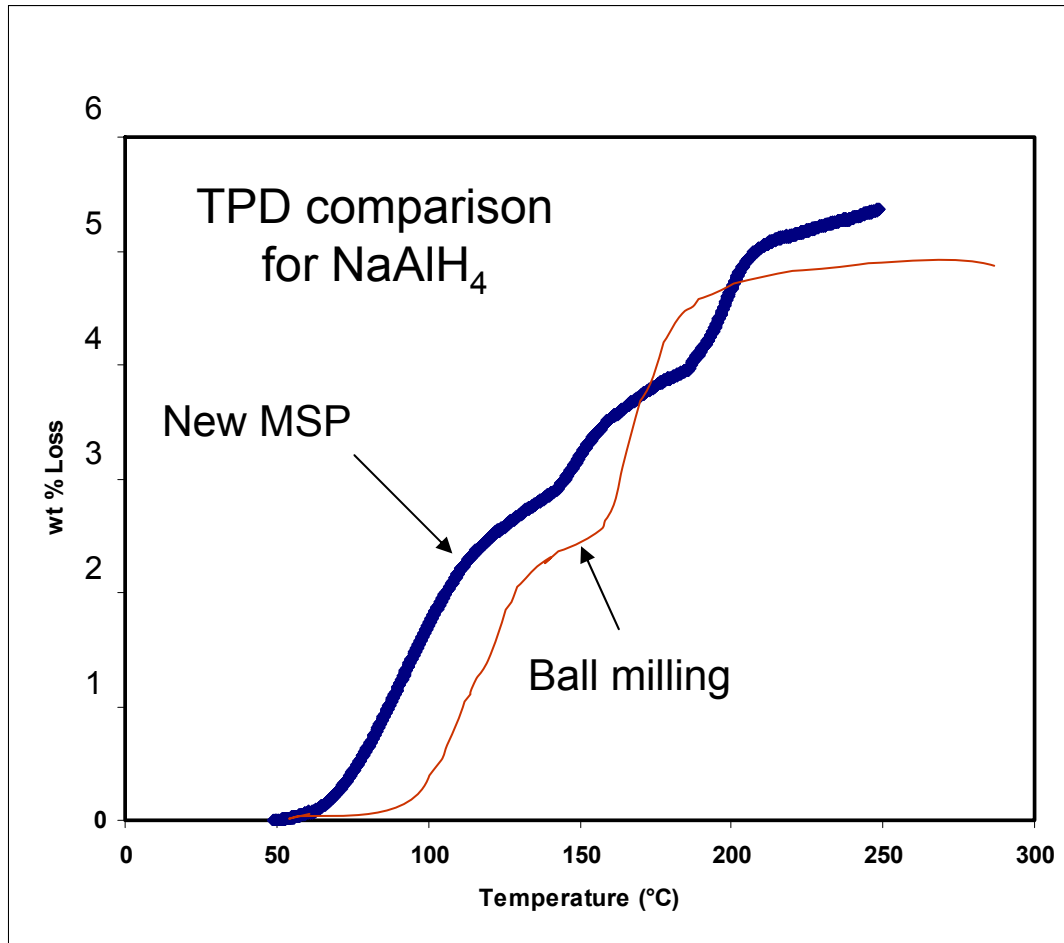
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- **New Molten State Process was found to both:**

- 1- Enhance Kinetics and

- 2- Lead to Formation of New Complexes

# Enhanced Kinetics



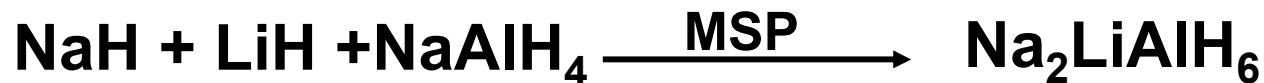


# Reported Alanate Complexes

Composition	Mol. Wt.	Wt.%H2
$\text{Be}(\text{AlH}_4)_2$	71.04	8.45
$\text{Mg}(\text{AlH}_4)_2$	86.33	6.95
$\text{Ca}(\text{AlH}_4)_2$	102.11	5.88
$\text{Sr}(\text{AlH}_4)_2$	149.65	4.01
$\text{LiAlH}_4$	37.95	7.91
$\text{NaAlH}_4$	54.00	5.56
$\text{KAlH}_4$	70.10	4.28
$\text{CsAlH}_4$	171.13	1.75
$\text{Ti}(\text{AlH}_4)_4$	171.95	8.14
$\text{AlH}_3$	30.00	10.0

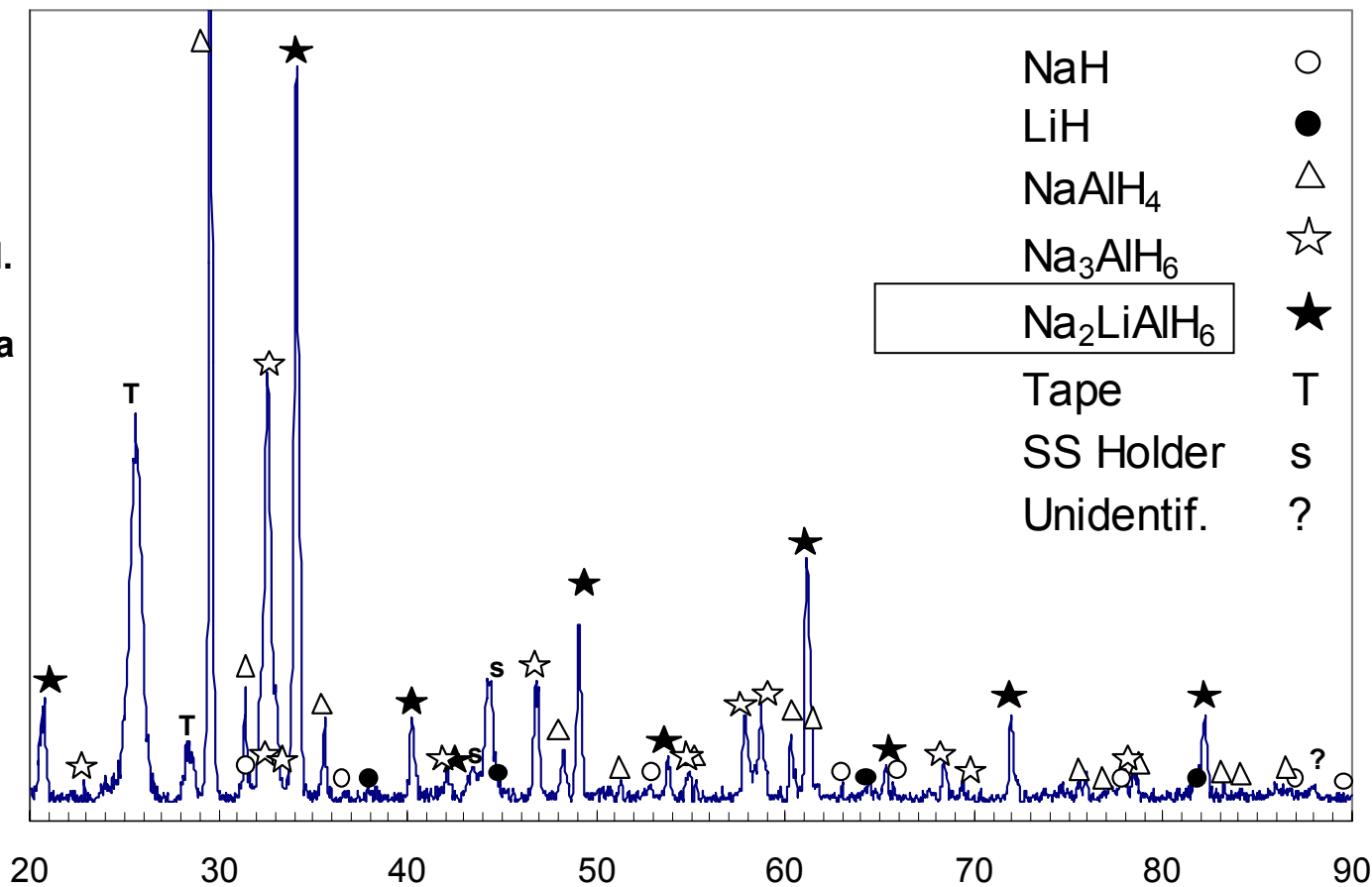
# Proof of Concept

# Formation of Complexes, MSP



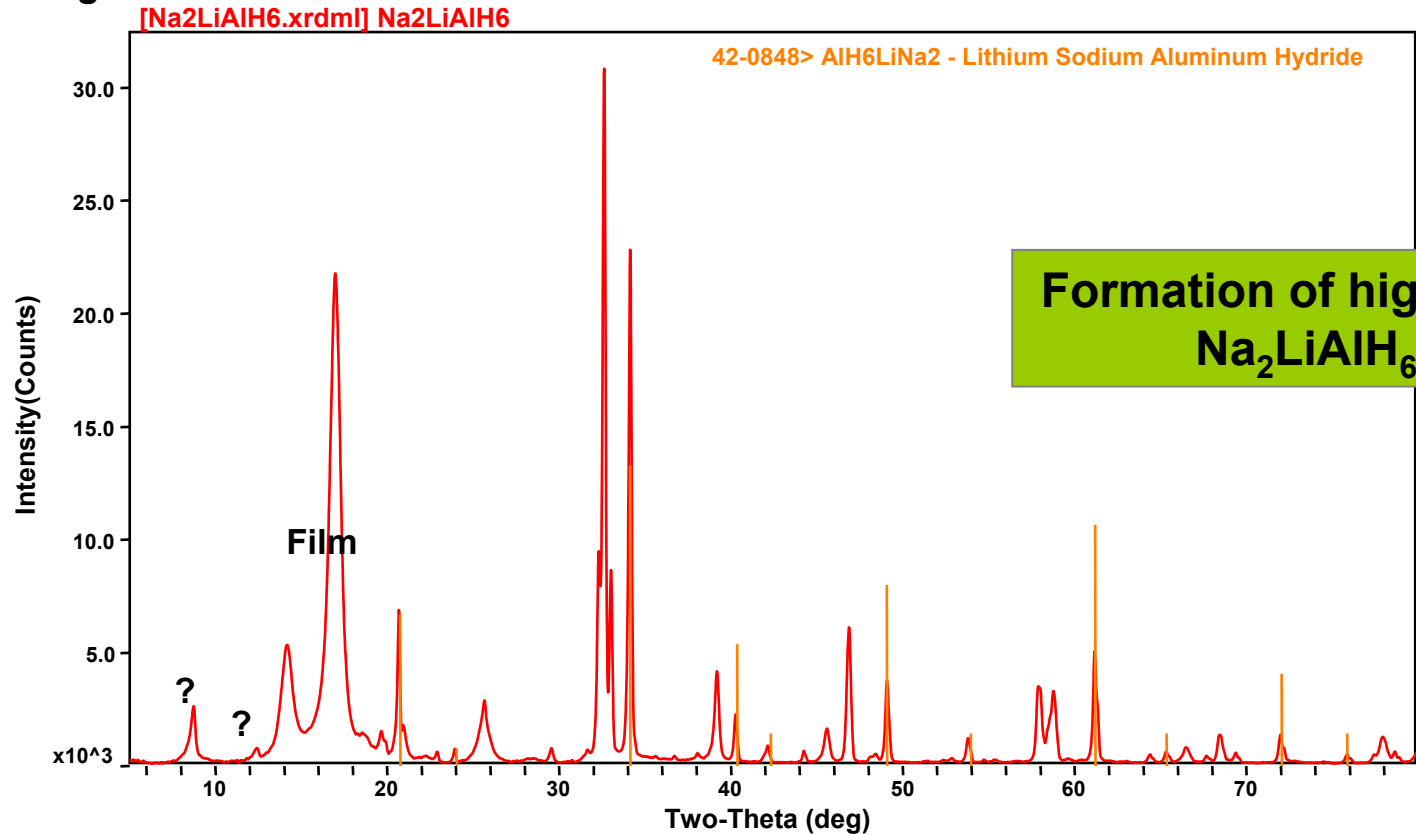
At 3000 psi hydrogen pressure and 190 deg C temperature  $\text{Na}_2\text{LiAlH}_6$  was formed.

Li atom substituted Na (no stirring)



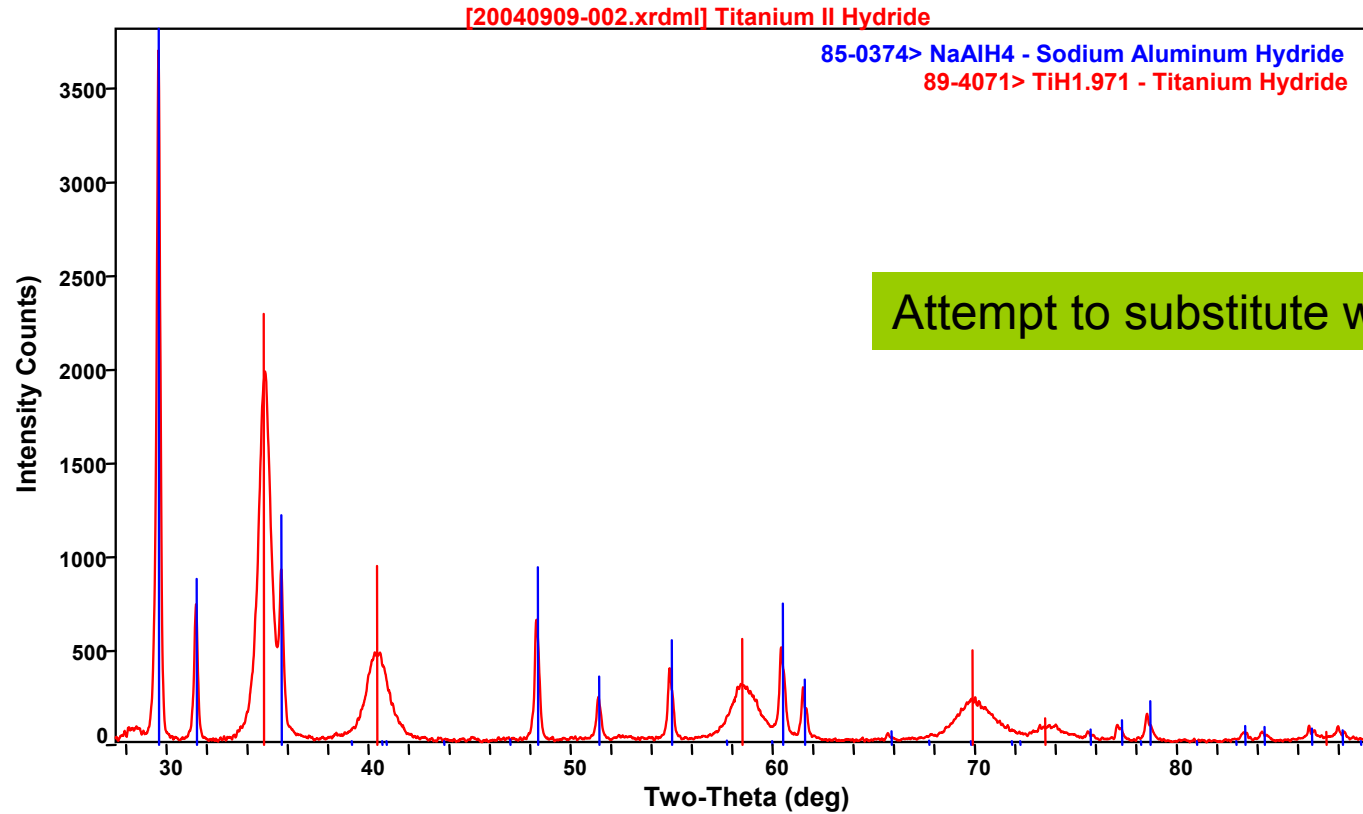
# Formation of Complexes

With Stirring



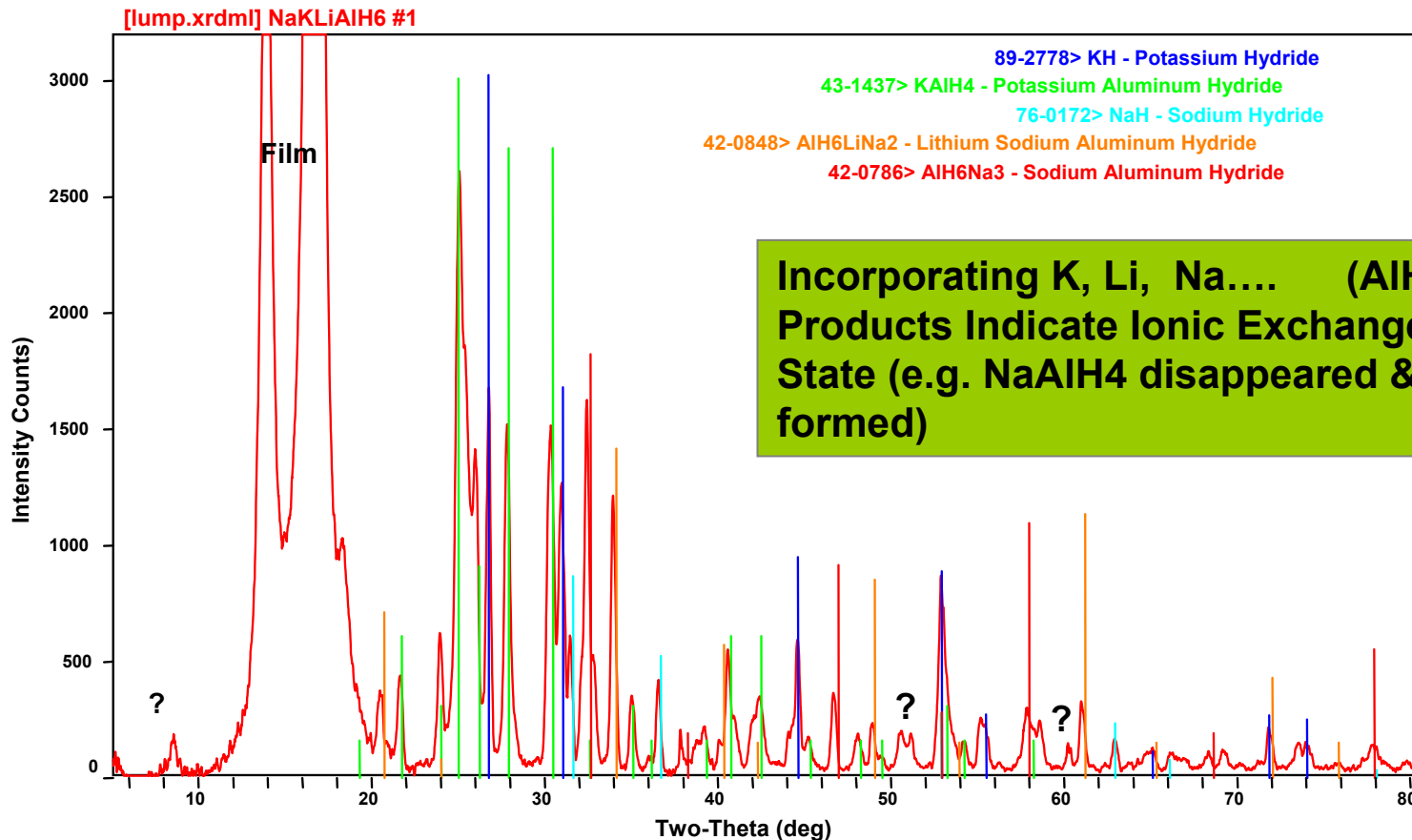
“Synthesis and crystal structure of Na<sub>2</sub>LiAlD<sub>6</sub>” *J. Alloys & Compounds In Press*, Nov. 2004  
H.W. Brinks, B.C. Hauback, C.M. Jensen and R. Zidan

# Formation of Complexes



# Identifying the possibilities of elemental exchange in molten state

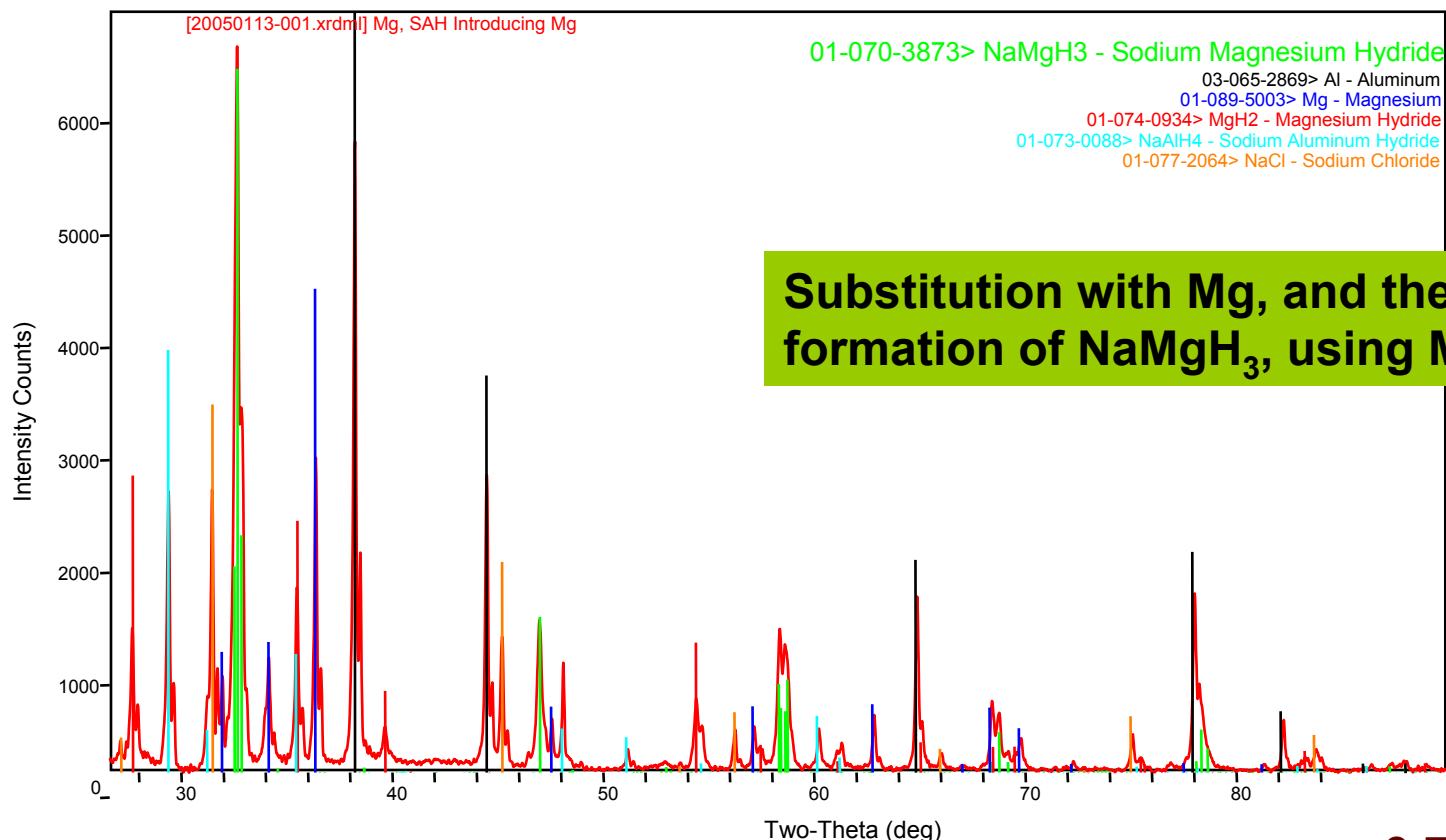
# Formation of Complexes



Some peaks could not be identified

# Recognizing the formation of $\text{NaMgH}_3$ and its reaction with $\text{NaAlH}_4$

# Formation of Complexes



Substitution with Mg, and the formation of  $\text{NaMgH}_3$ , using MSP

Once optimized reversible reaction was realized:



3.7 wt. %H

@150 °C



# Reviewer's Comments

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- **SRNL Project was not separately reviewed in 2004 - it was reviewed as part of the overall UTRC Project (ST6)**
- **Overall Project was a new FY04 start and received a favorable review.**
- **Only specific SRNL related comment was on Molten State Process - asking if it had been tried with SAH – it was tried in 2005 with very encouraging results.**

# Summary of Accomplishments

- **New Molten State Process was successfully demonstrated**
- **Kinetics of  $\text{NaAlH}_4$  was enhanced**
- **Elemental substitution capability (Li, K, Mg) was shown**
- **Novel compositions ( $\text{Na}_2\text{LiAlH}_6$  and  $\text{NaMgH}_3$ ) were made**
- **Utilized UTRC modeling effort to guide material development**
- **Achieving a better understanding of the mechanism of formation of these materials**



# Future Work

- **Continue transition metal aluminum hydrides containing Ti, Zr, Mn, Fe and alkaline and alkaline earth aluminum hydrides substitutions**
- **Optimize MSP yield for most promising candidate materials**
- **Perform thermodynamic measurement on most promising candidate materials and compare to DOE Storage Goals**
- **Continue to utilize UTRC modeling efforts and SRNL spectroscopic and structural studies to guide material development**
- **Continue to develop a better understanding of mechanism of formation and decomposition of these materials**

# Recent Publications and Presentations

## Publications:

“Synthesis and crystal structure of  $\text{Na}_2\text{LiAlD}_6$ ” *J. Alloys and Compounds Volume 392, Issues 1-2, 19 April 2005, Pages 27-30*, H.W. Brinks, B.C. Hauback, C.M. Jensen and R. Zidan

“Synergistic effects of co-dopants on the dehydrogenation kinetics of sodium aluminum hydride” *J. alloys and compounds Volume 391, Issues 1-2, 5 April 2005, Pages 245-255*  
J. Wang, A.D. Ebner, R. Zidan and J.A. Ritter

“Effect of graphite as a co-dopant on the dehydrogenation and hydrogenation kinetics of Ti-doped sodium aluminum hydride” *J. Alloys and Compound, in press*, Jun Wang, Armin D. Ebner, Tanya Prozorov, Ragaiy Zidan and James A. Ritter

## Presentations:

•Hydrogen Economy Workshop, *Invited Speaker, for the Department of Energy*, (1)Hydrogen Storage R&D Key Issues for the Hydrogen Economy, (2)Solid-State Hydrogen Storage Systems Cairo Egypt January 31 – February 2, 2005

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