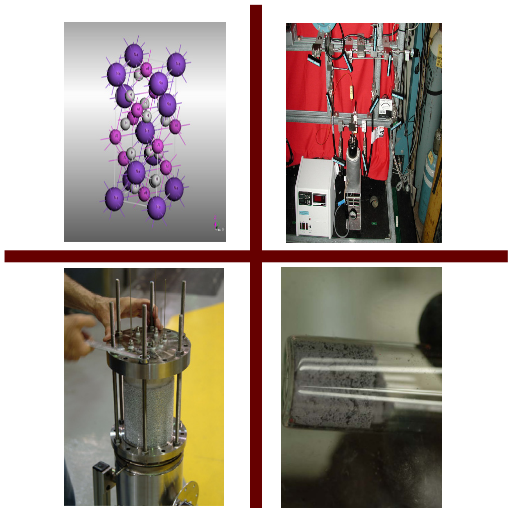
Development and Characterization of Complex Hydrides

Molten State Processing
in Support of UTRC Material Discovery Project



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SAVANNAH RIVER NATIONAL LABORATORY

We Put Science To Work

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Savannah River National Laboratory

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Project ID # STP58

This presentation does not contain any proprietary or confidential information

WSRC-MS-2005-00259

Overview

Timeline

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

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

Budget

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

Partners

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

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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 $Na_yM_{+ix}(AlH_4)_{y+ix}$ based on NaH, AlH_3, transition metal or rare earth (M) hydrides.
- Material capable of reversibly storing H_2 > 7.5 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.

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Approach

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.

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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

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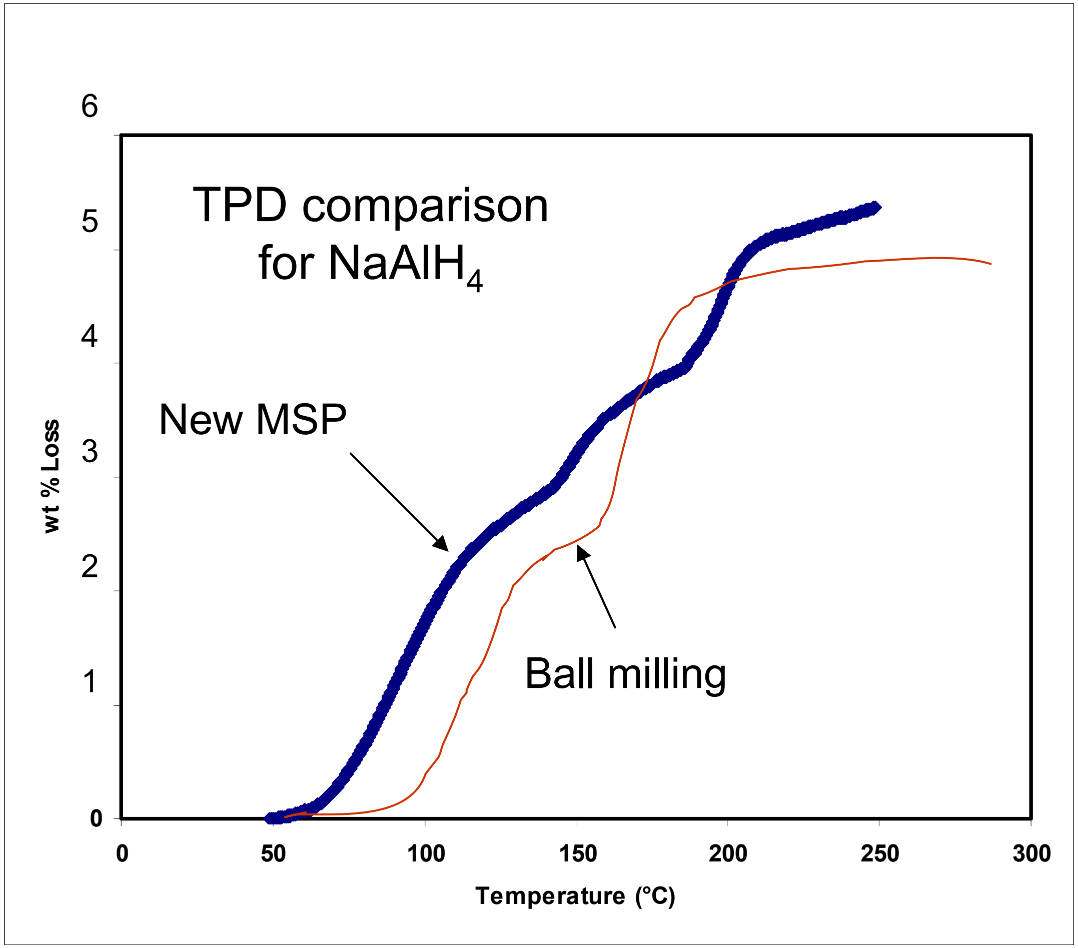
Material Development

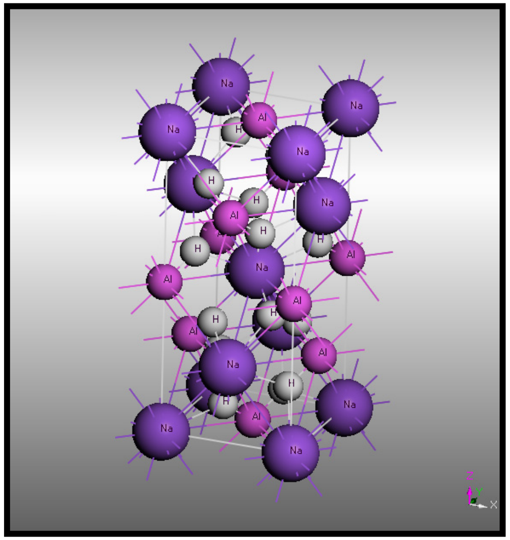
- **New Molten State Process was found to both:**

  1- Enhance Kinetics and

  2- Lead to Formation of New Complexes

Enhanced Kinetics





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Reported Alanate Complexes

Composition	Mol. Wt.	Wt.%H2
$Be(AlH_4)_2$	71.04	8.45
$Mg(AlH_4)_2$	86.33	6.95
$Ca(AlH_4)_2$	102.11	5.88
$Sr(AlH_4)_2$	149.65	4.01
$LiAlH_4$	37.95	7.91
$NaAlH_4$	54.00	5.56
$KAlH_4$	70.10	4.28
$CsAlH_4$	171.13	1.75
$Ti(AlH_4)_4$	171.95	8.14
AlH_3	30.00	10.0

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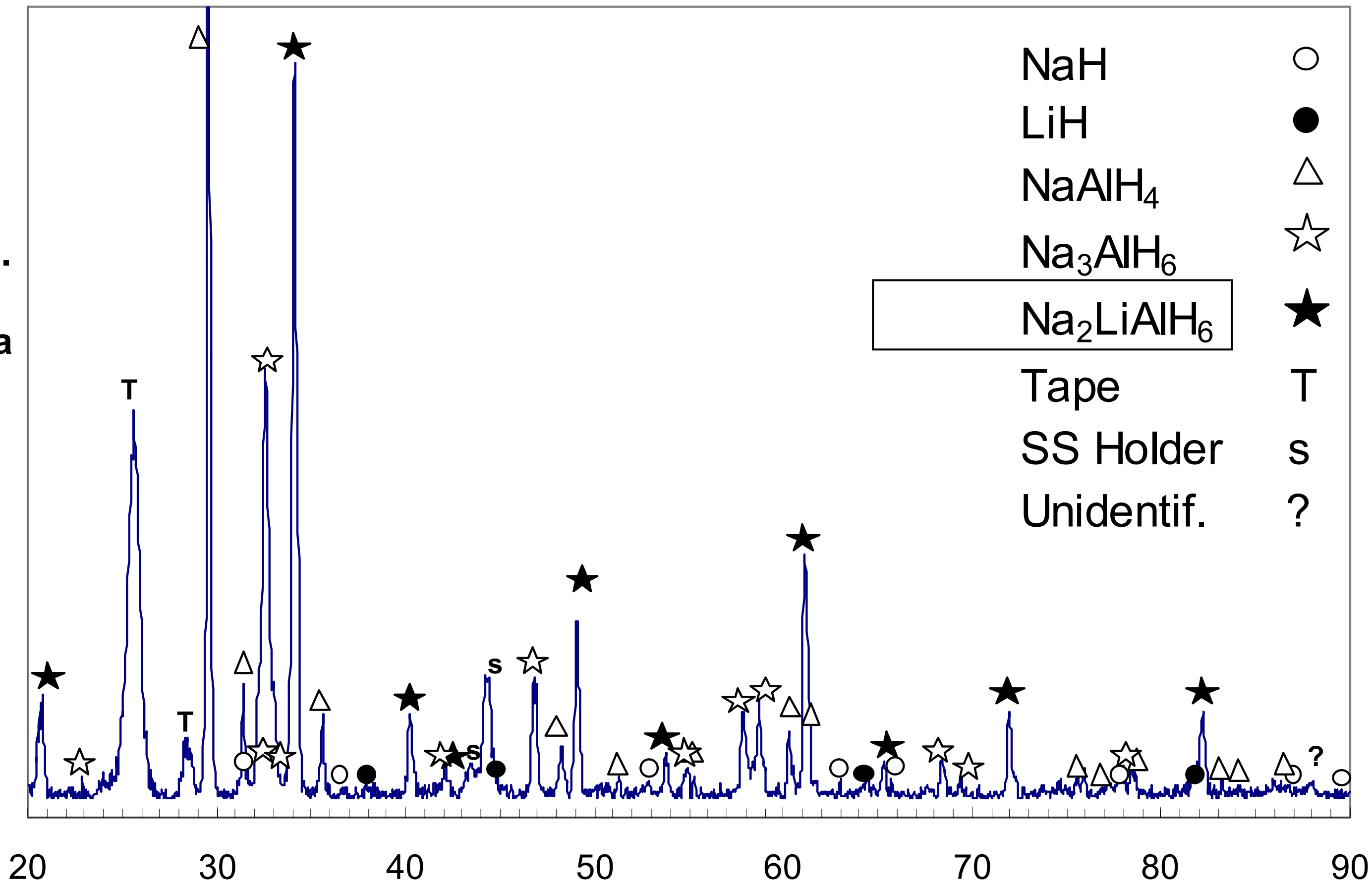
Proof of Concept

Formation of Complexes, MSP

$$NaH + LiH + NaAlH_4 \xrightarrow{MSP} Na_2LiAlH_6$$

At 3000 psi hydrogen pressure and 190 deg C temperature Na_2LiAlH_6 was formed.

Li atom substituted Na (no stirring)



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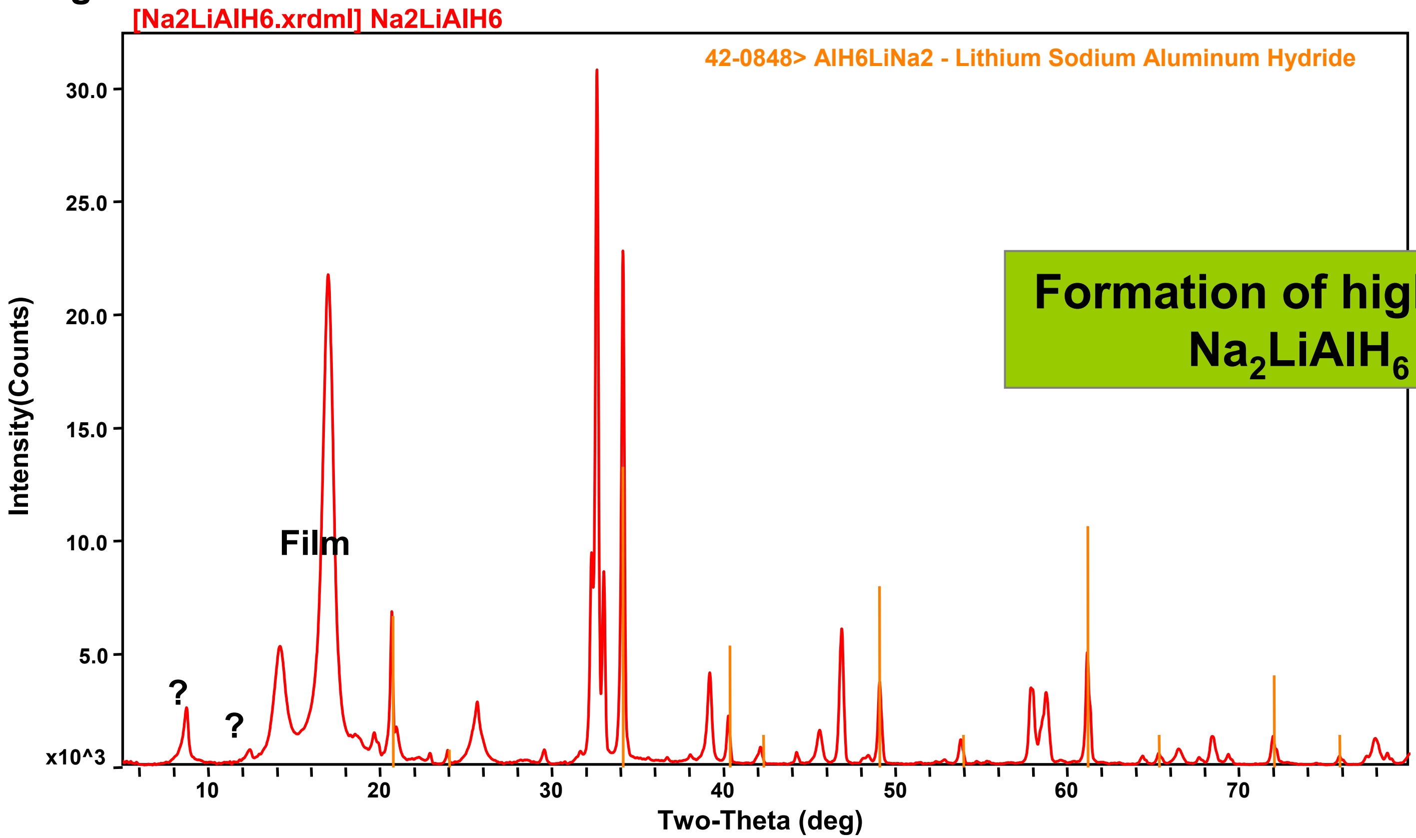
Formation of Complexes

With Stirring



Formation of high yield Na_2LiAlH_6

"Synthesis and crystal structure of Na_2LiAlD_6" ***J. Alloys & Compunds In Press, Nov. 2004***
H.W. Brinks, B.C. Hauback, C.M. Jensen and R. Zidan

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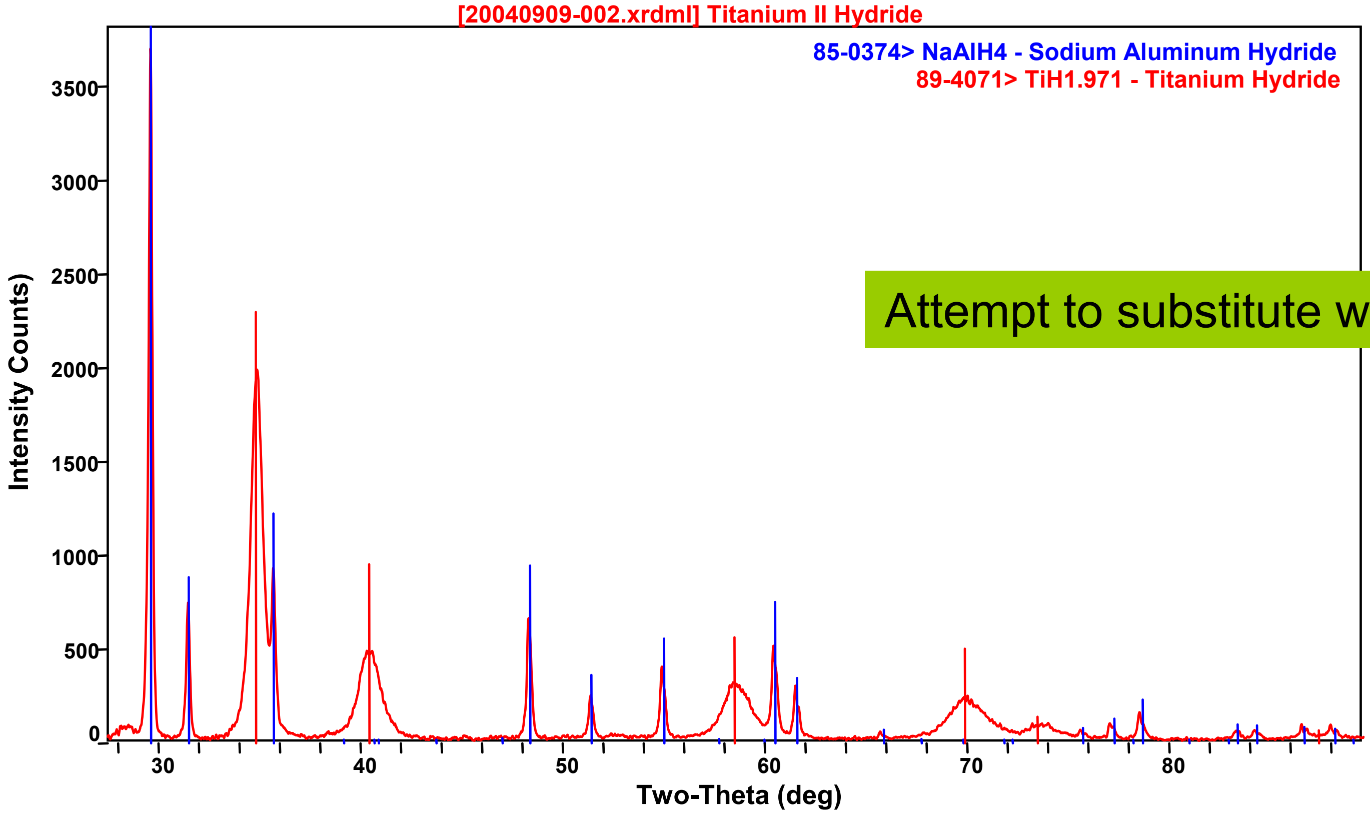
Formation of Complexes



Attempt to substitute with Ti

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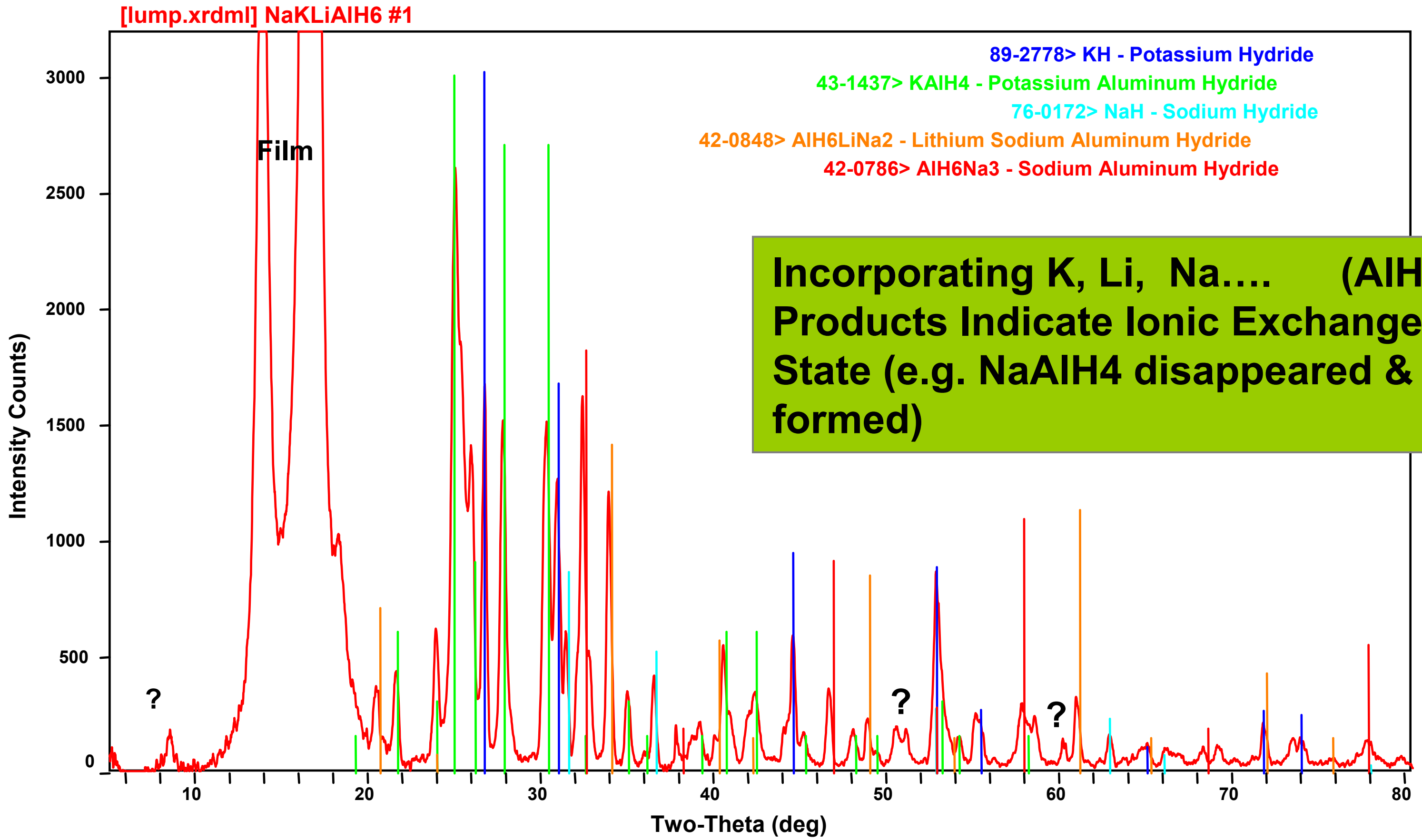
Identifying the possibilities of elemental exchange in molten state

Formation of Complexes



Incorporating K, Li, Na…. (AlH_4) Products Indicate Ionic Exchange in Molten State (e.g. NaAlH4 disappeared & KAlH4 was formed)

Some peaks could not be identified

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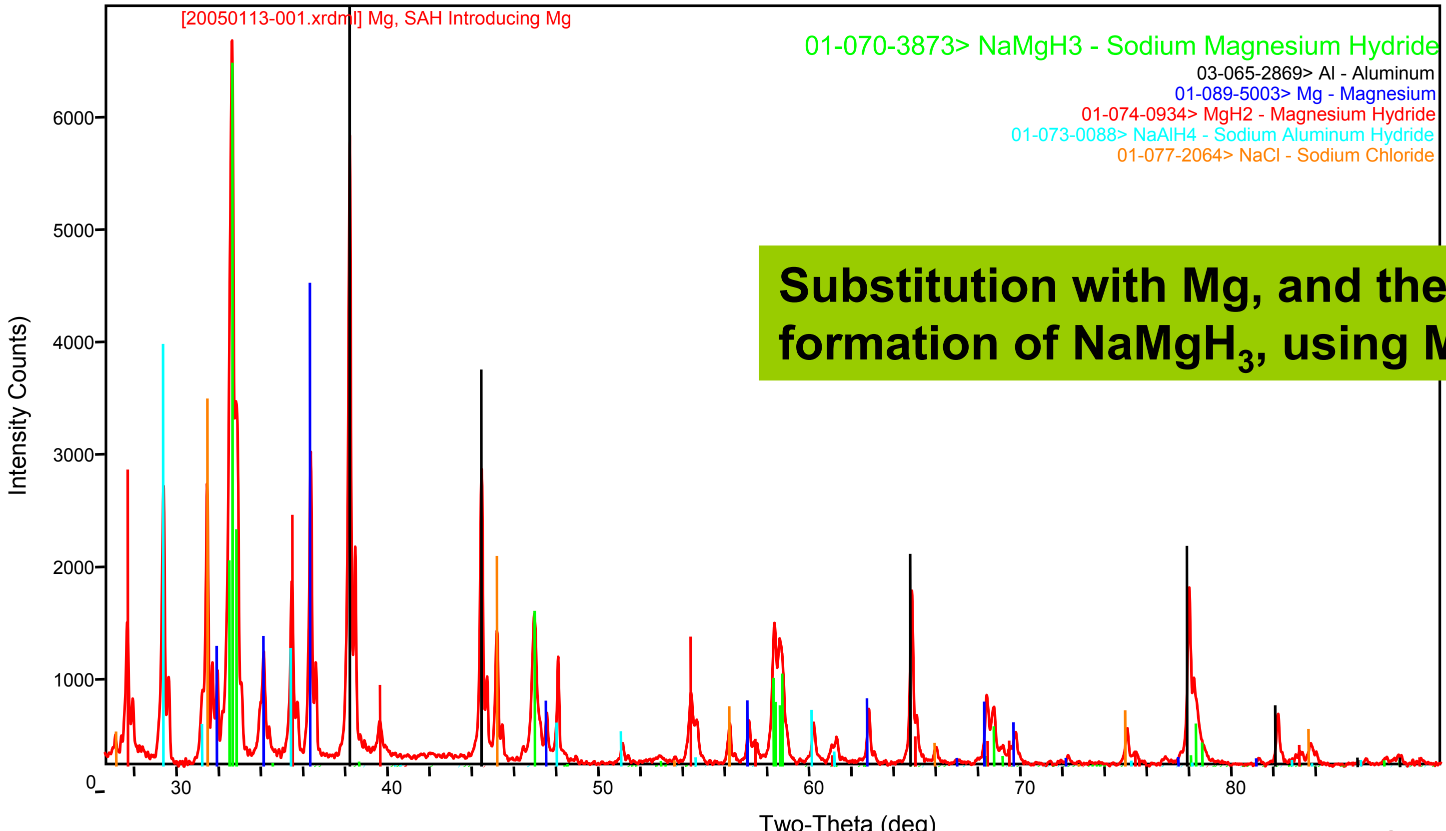
Recognizing the formation of $NaMgH_3$ and its reaction with $NaAlH_4$

Formation of Complexes

$NaAlH_4$ + (excess) Mg + Al + H_2 ⟶ MgH_2 + Al + Mg + $NaAlH_4$ + $NaMgH_3$



Substitution with Mg, and the formation of $NaMgH_3$, using MSP

Once optimized reversible reaction was realized:

$NaAlH_4 + MgH_2 \rightleftharpoons NaMgH_3 + Al + 3/2\ H_2 \uparrow$

3.7 wt. %H

@150 °C

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Reviewer's Comments

- 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.

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Summary of Accomplishments

- **New Molten State Process was successfully demonstrated**
- **Kinetics of $NaAlH_4$ was enhanced**
- **Elemental substitution capability (Li, K, Mg) was shown**
- **Novel compositions (Na_2LiAlH_6 and $NaMgH_3$) were made**
- **Utilized UTRC modeling effort to guide material development**
- **Achieving a better understanding of the mechanism of formation of these materials**

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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

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Recent Publications and Presentations

Publications:

"Synthesis and crystal structure of Na2LiAlD6" ***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**

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