METAL HYDRIDE CENTER OF EXCELLENCE

Development of Reversible Hydrogen Storage Alane

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SAVANNAH RIVER NATIONAL LABORATORY

We Put Science To Work

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Project ID#: STP20

Overview

Timeline

- Project Start: March 2005
- Project End: TBD
- Percent Complete: <5% new start

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 Project Funding: $200K/yr
  - DOE Share: 100%
  - Contractor Share: NA
- $0 receive in FY04 (new start)
- $200K received in FY05

Partners

- Brookhaven National Laboratory
- Sandia National Laboratory
- University of Hawaii and other CoE partners as needed

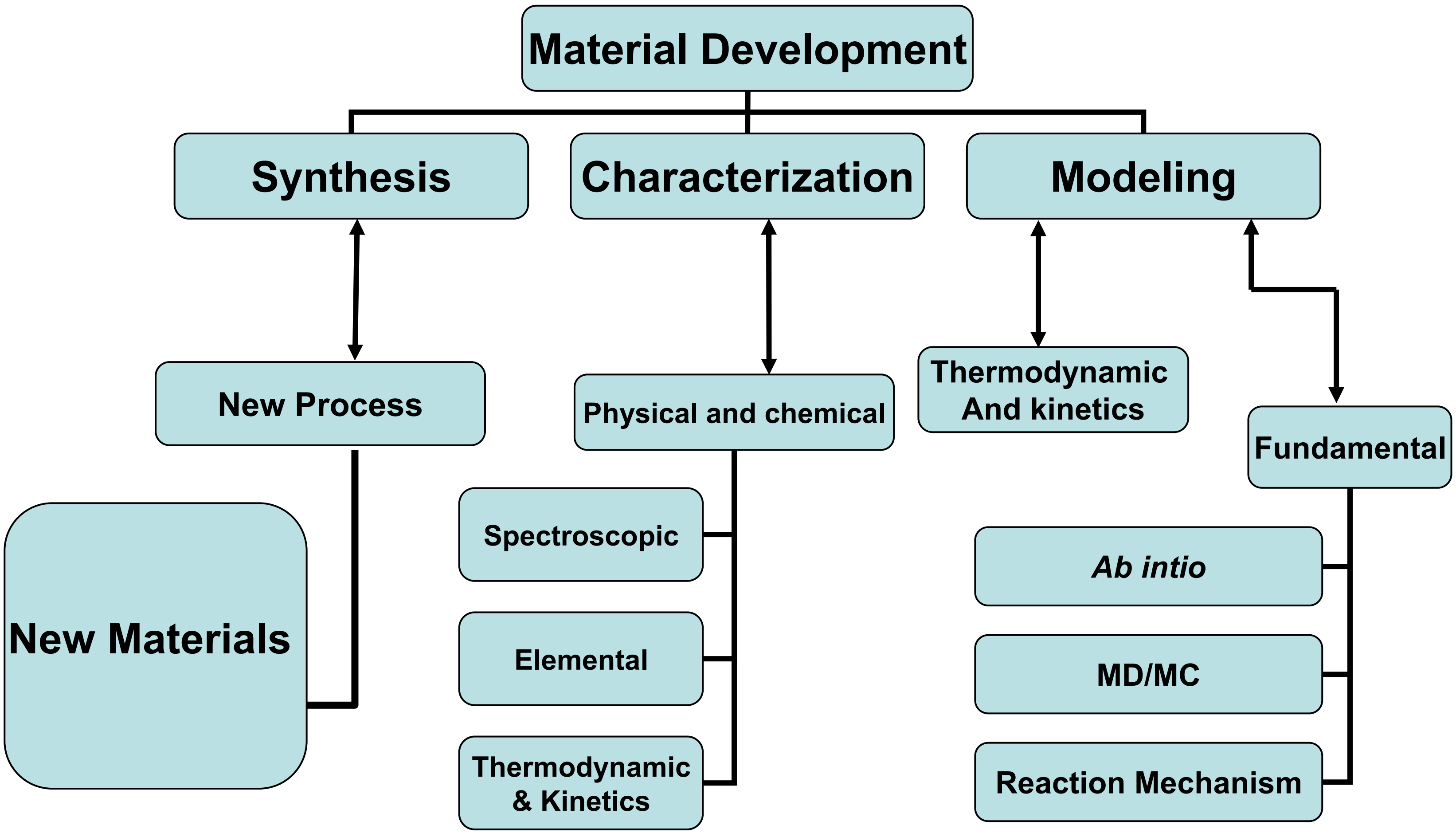
Objective

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

Specific Objectives

- Design and fabricate a novel high pressure cell to efficiently charge aluminum hydride (alane)
- Test and evaluate feasibility of cell for alane charging
- Characterize and analyze charged alane materials for structure, purity and yield

SRNL Approach



Reported High Capacity Al 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

Alane

AlH_3= 10% wt

•Savannah River leads Hydrogen Charging

•Brookhaven leads Hydrogen Discharging

Some sample preparation, exchange and confirmation of structures will be done by others.

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Alane Formation

- Alane formation, from the elements, has been reported to occur under very high pressure conditions
- Or plasma Conditions
- Or by non-economical chemical reactions
- Competing reaction can lead to unstable phases
- Innovative methods are needed to recharge

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SRNL Program Plan

Alanes

- **Task 1 - High Pressure Cell Design and Fabrication**
  A high pressure cell to synthesize alanes at reasonable operating conditions will be designed and fabricated. The cell will take advantage of a new SRNL design (patent pending).

- **Task 2 – High Pressure Cell Testing and Material Synthesis**
  The new cell will be installed in the SRNL high pressure laboratory and synthesis operations will be initiated. The goal of this task is to demonstrate a new process for producing stable high capacity alanes at reasonable operating conditions. The key to the first year effort is the development of stable alane materials. A GO NO GO decision will be made after the first year with respect to the potential of using this process for developing suitable high capacity hydrogen storage materials.

- **Task 3 – Characterization**
  Structural characterizations and physical property analyses will be employed to identify material purity and yield. X-ray diffraction and differential scanning calorimetry (DSC) analyses will be the primary tools. X-ray diffraction will be used to determine phase structure, lattice parameters and a preliminary assessment of the volume fractions of the material produced.

Summary of Progress and Results

- Basic thermodynamic and diffusion considerations were made and preliminary cell design is under way
- Preliminary alane materials were characterized (SEM, XRD)
- Preliminary material were evaluated for hydrogen release (TGA, TPD TVA)
- High pressure test system capabilities were established

Basic Thermodynamics

- **Pressure and chemical potential**

$$\Delta G = \Delta H - T\,\Delta S$$

$$RT \ln f = \Delta H - T\,\Delta S$$

$$\ln P = \Delta H / RT - \Delta S / R \text{ (low pressure)}$$

- **Phase and competing reactions**

Dehydrided Phase will be used

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Diffusion of Hydrogen

$$\frac{\partial C}{\partial t} = \nabla(D\nabla C) = \nabla D.\nabla C + \underline{\underline{D\nabla^2 C}}$$

In one dimension :

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + \frac{\partial D}{\partial x}\frac{\partial C}{\partial x}$$

or

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + \frac{\partial D}{\partial C}\left(\frac{\partial C}{\partial x}\right)^2$$

Non-linearity hinders rate of diffusion

Diffusion of Hydrogen

Periodic and non-periodic systems

Fraction of occupied state expressed by Fermi - Dirac distrubtion :

$$C = \sum_i \frac{\delta(E_i - E_m)}{1 + \exp\left(\frac{E_i - \mu}{KT}\right)}$$

$$\delta(E_i - E_m) = \lim_{\sigma \to 0}\left\{\frac{1}{\sqrt{\pi}\sigma}\exp\left(\frac{(E_i - E_m)^2}{\sigma^2}\right)\right\}$$

In general

$$C = \frac{1}{\sqrt{\pi}\sigma}\sum_i \frac{\exp\left(\frac{(E_i - E_m)^2}{\sigma^2}\right)}{1 + \exp\left(\frac{E_i - \mu}{KT}\right)} \quad \sigma \to 0 \text{ for periodic structure}$$

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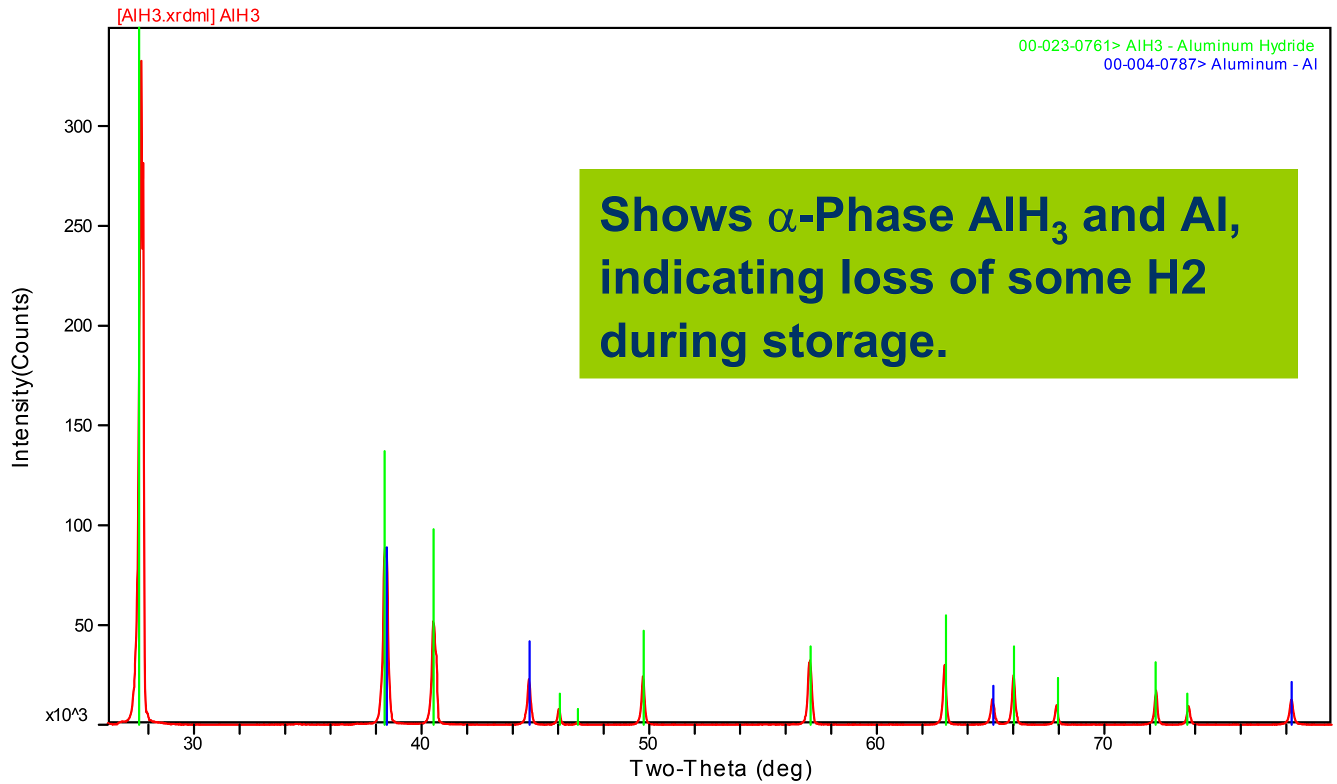
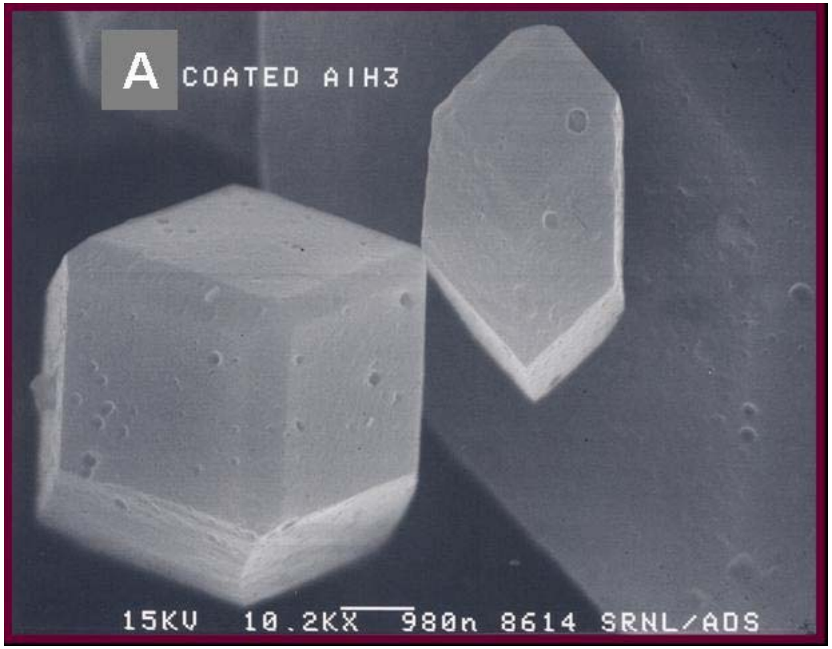
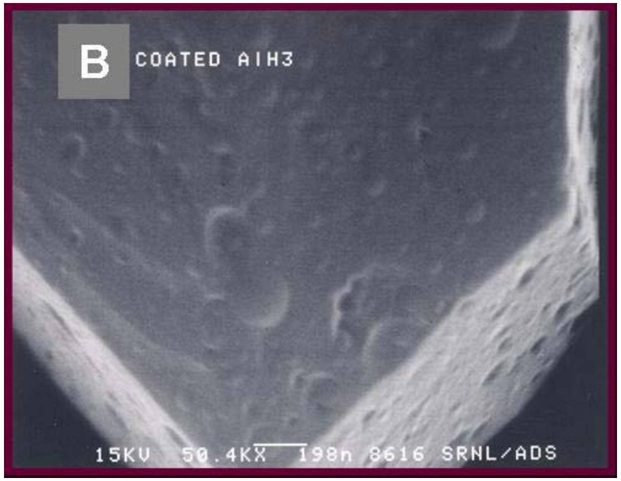
Structure Characterization - XRD

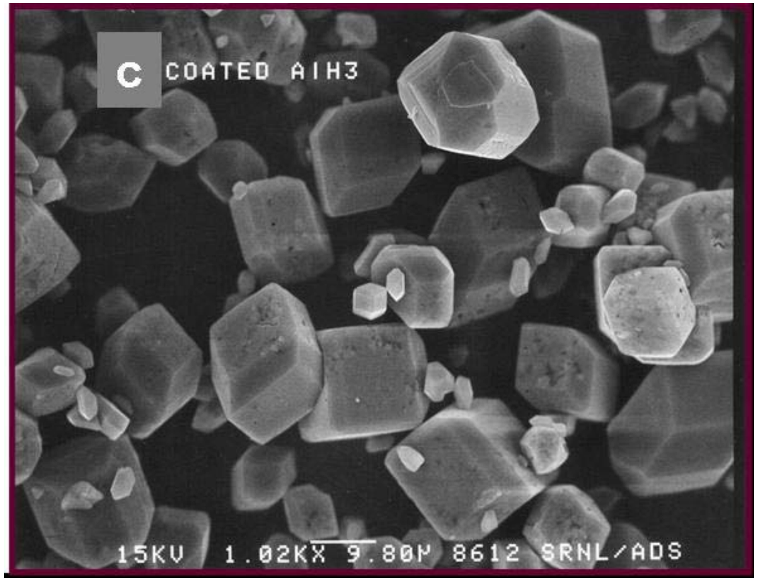


Sample is polymer coated, obtained from United Technology Research Center (UTRC)

SEM Images of Alane







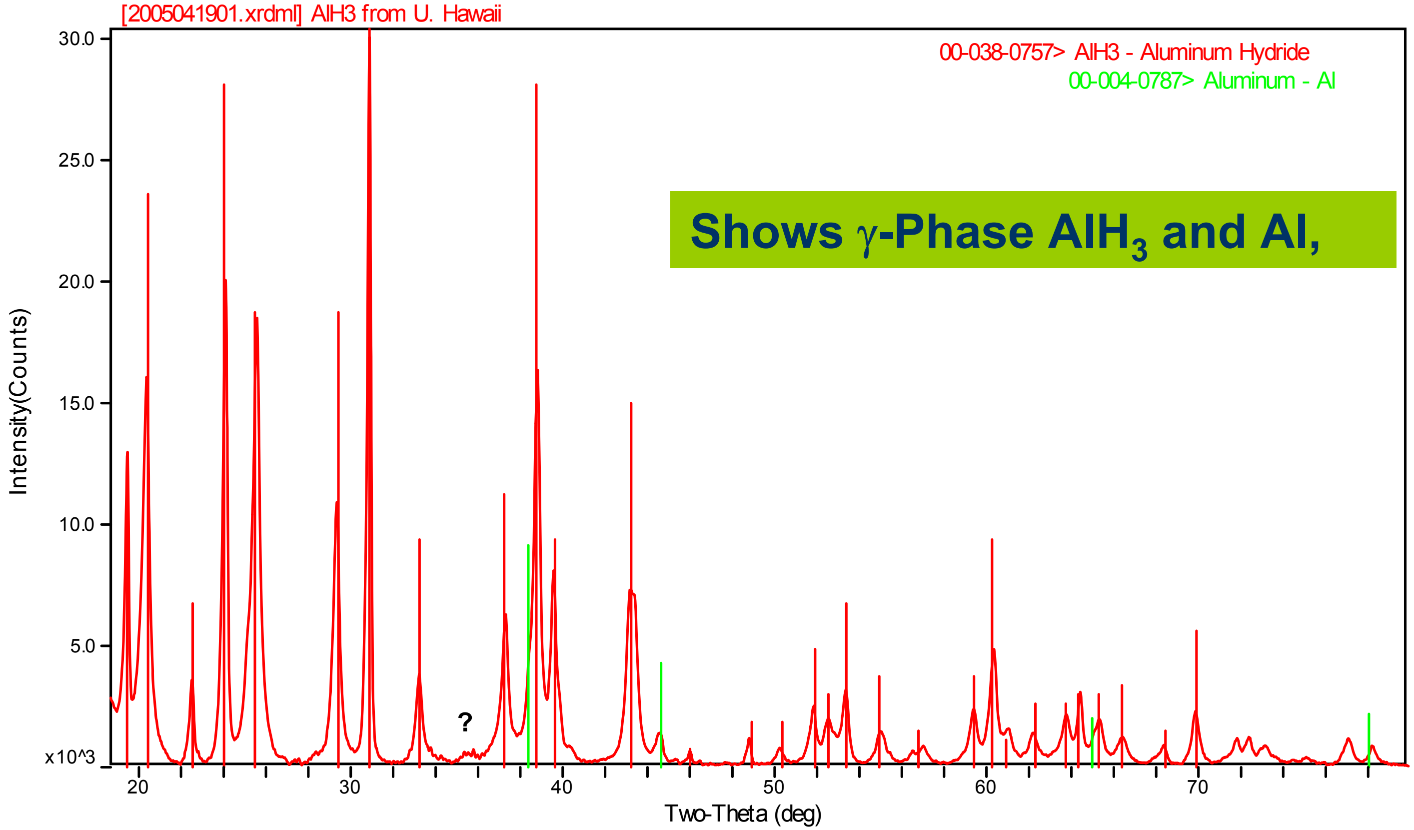
A. SEM image showing the Crystalline shape of AlH_3

B. The surface of the crystals shows pitted areas, indicating hydrogen leak

C. SEM image showing the particle size

Sample is polymer coated, obtained from United Technology Research Center UTRC

Structure Characterization - XRD



Sample was chemically prepared and provided by Professor Craig Jensen from University of Hawaii

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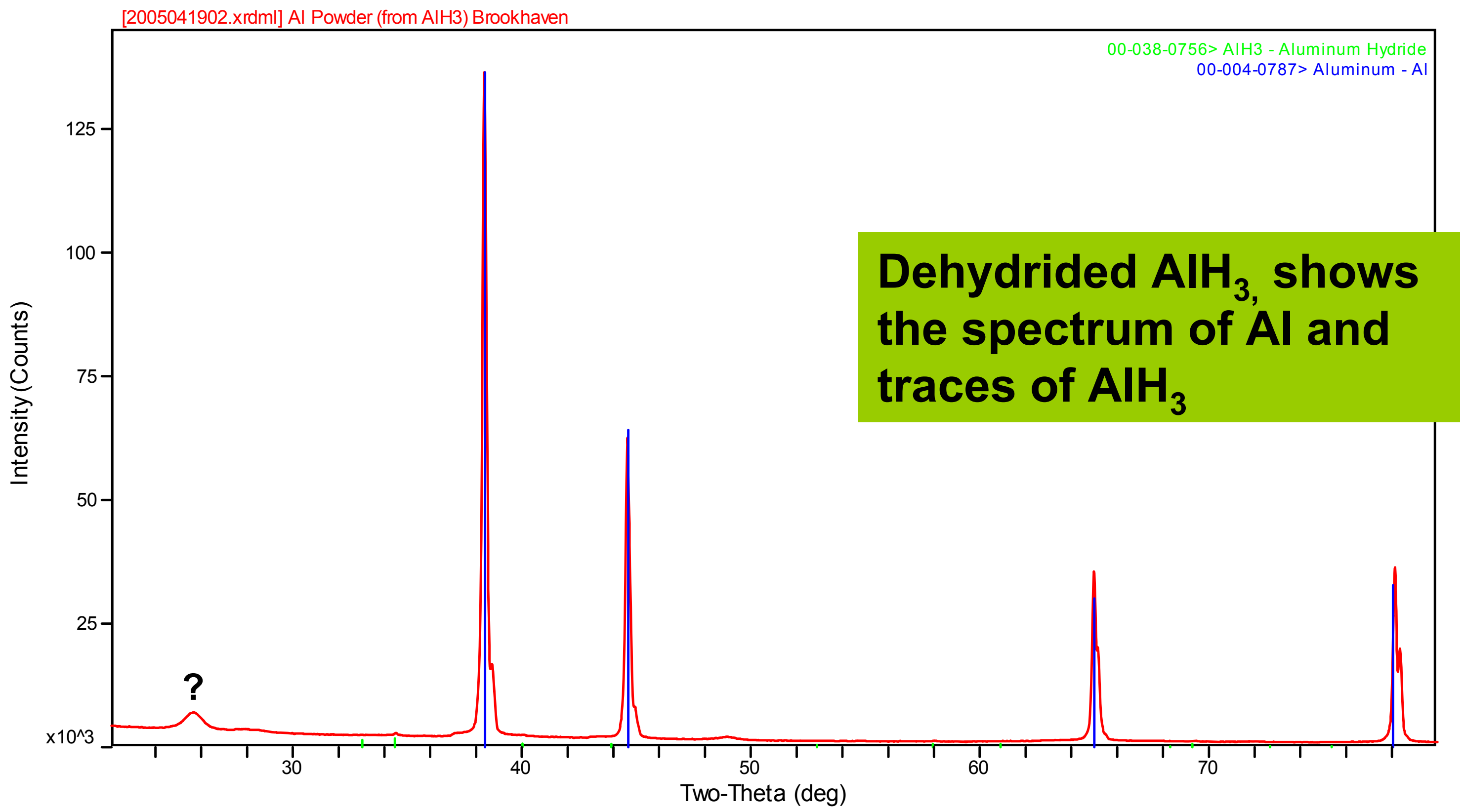
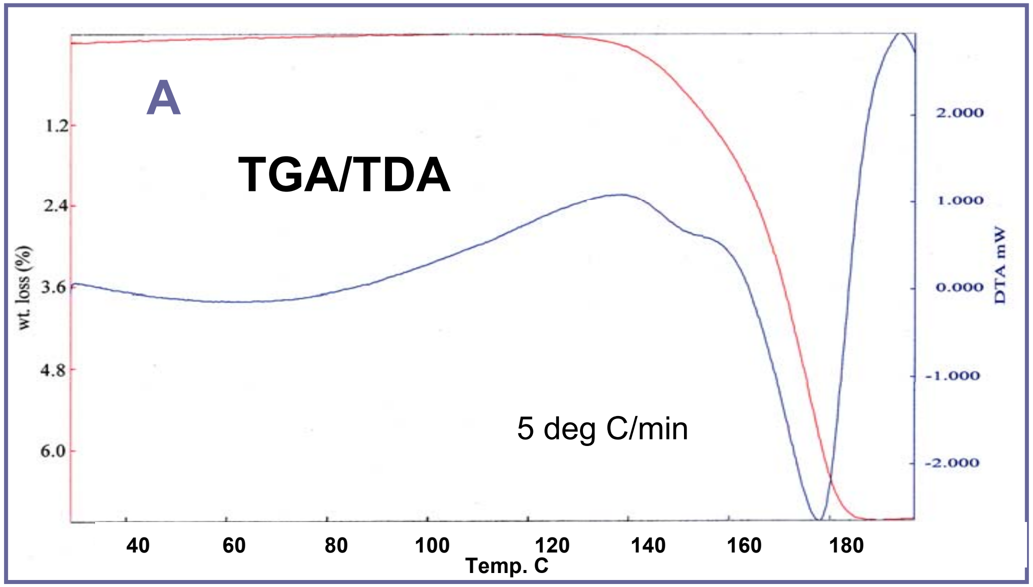
Structure Characterization - XRD



Dehydrided AlH_3, shows the spectrum of Al and traces of AlH_3

Sample was provided by Brookhaven National Laboratory (BNL)

Hydrogen Release from Alane



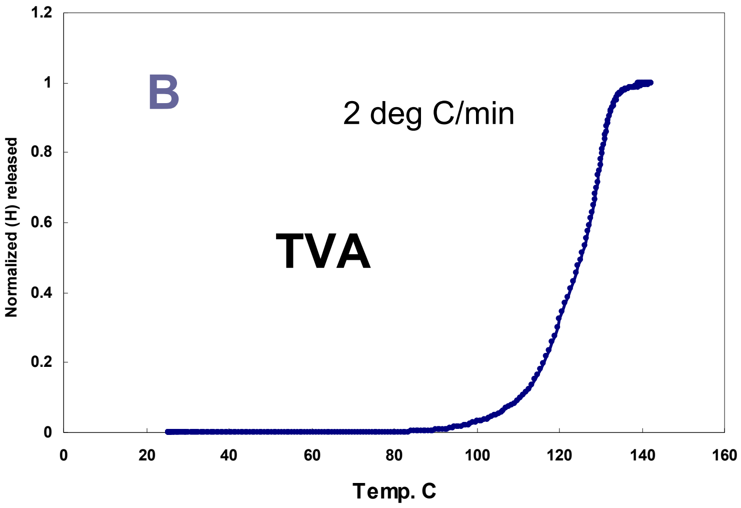
Weight % Released = 7.2 H

Heat of Reactions = -7.6 kJ/mol

Thermal Programmed Desorption (TPD) of hydrogen from AlH_3 Using:

A) Thermogravimetric analyzer (TGA)

B) Thermovolumetric analyzer (TVA)



High Pressure Characterization System

Future Work

- Complete cell design & fabrication (SRNL patent pending)
- Install cell in SRNL high pressure laboratory and initiate charging tests.
- Perform structural characterization and physical property analyses to identify material purity and yield (XRD, DSC)
- Arrive at GO NO GO decision after first year on potential of process for producing suitable high hydrogen capacity storage materials
- If successful continue to develop and refine process for future deployment in collaboration with other CoE partners

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**