

Development of Reversible Hydrogen Storage Alane



Ragaiy Zidan*

**Kirk Shanahan, Steven Serkiz, Arthur Jurgensen, Ted Motyka
Savannah River National Laboratory
May 23-25, 2005**

Timeline

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

Budget

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

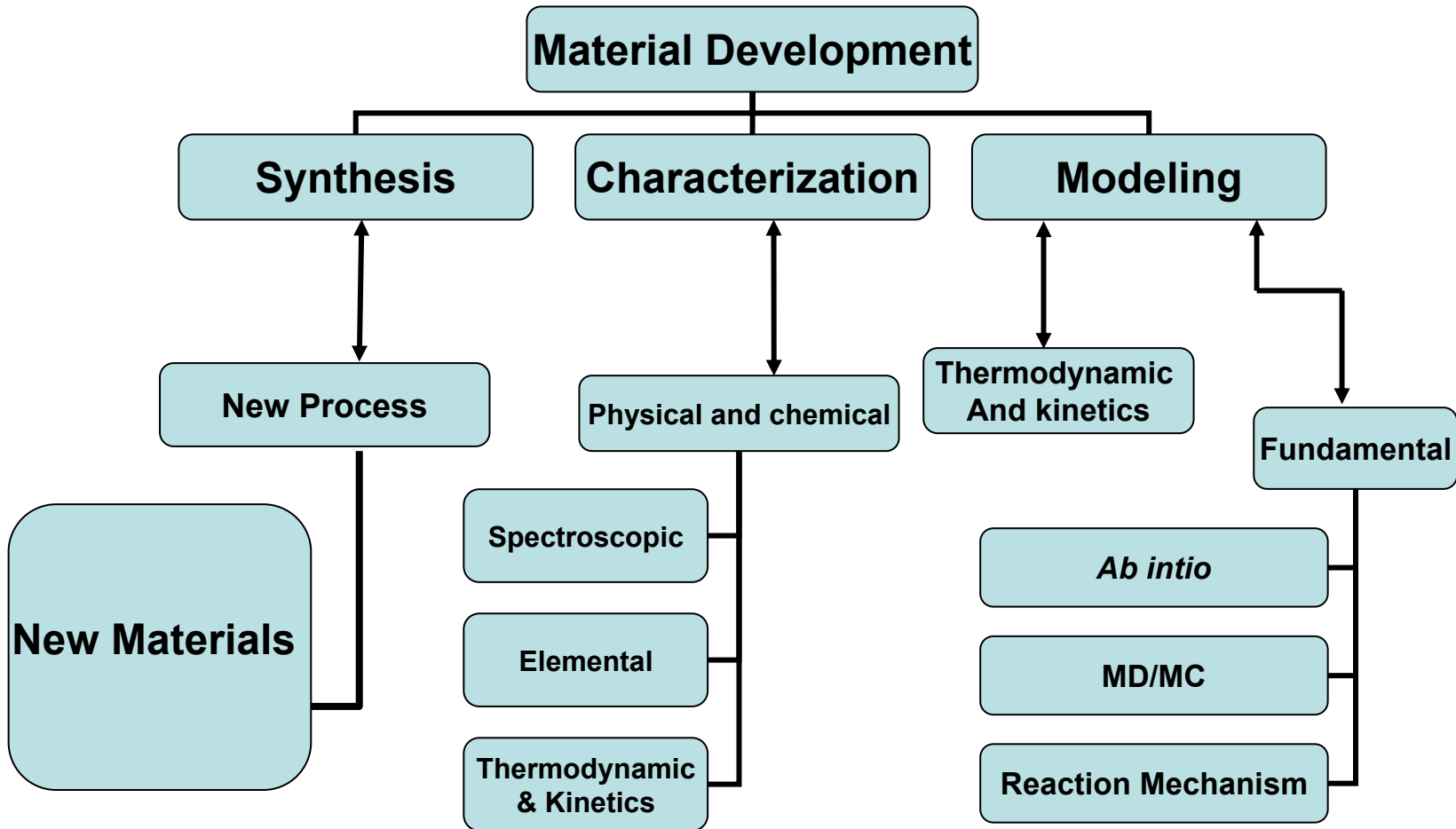
Partners

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

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

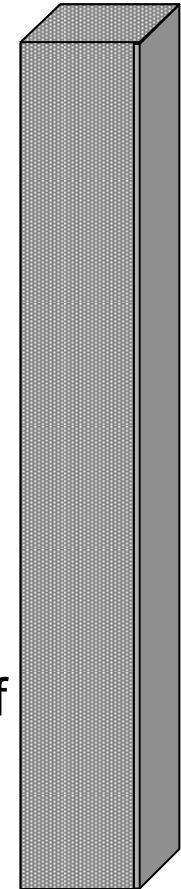
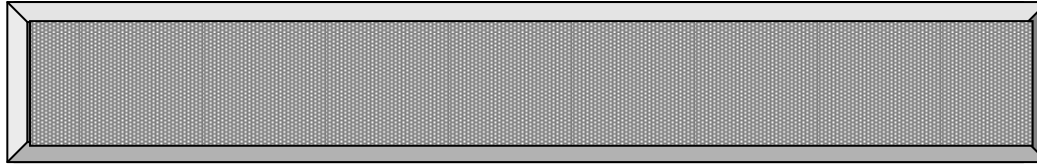
- **Design and fabricate a novel high pressure cell to efficiently charge aluminum hydride (alane)**
- **Test and evaluate feasibility of cell for alane charging**
- **Characterize and analyze charged alane materials for structure, purity and yield**



Reported High Capacity Al Complexes

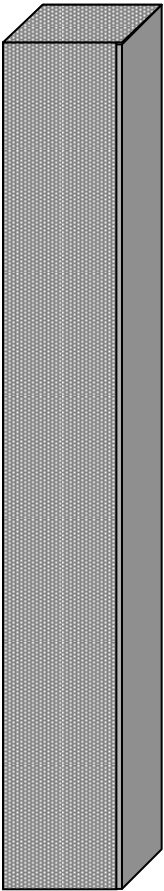
Composition	Mol. Wt.	Wt.%H ₂
Be(AlH ₄) ₂	71.04	8.45
Mg(AlH ₄) ₂	86.33	6.95
Ca(AlH ₄) ₂	102.11	5.88
Sr(AlH ₄) ₂	149.65	4.01
LiAlH ₄	37.95	7.91
NaAlH ₄	54.00	5.56
KAlH ₄	70.10	4.28
CsAlH ₄	171.13	1.75
Ti(AlH ₄) ₄	171.95	8.14
AlH ₃	30.00	10.0

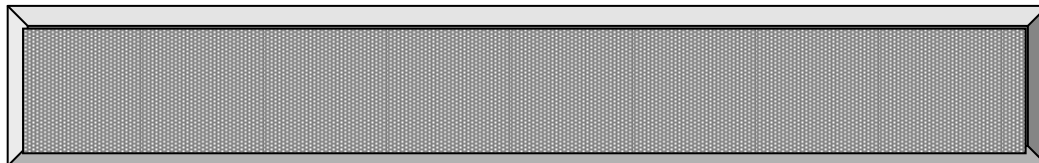
$\text{AlH}_3 = 10\% \text{ wt}$



- Savannah River leads Hydrogen Charging
- Brookhaven leads Hydrogen Discharging

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

- 
- 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



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**

- 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

Dehydrated Phase will be used

Diffusion of Hydrogen

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

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

Periodic and non-periodic systems

Fraction of occupied state expressed by Fermi - Dirac distribution :

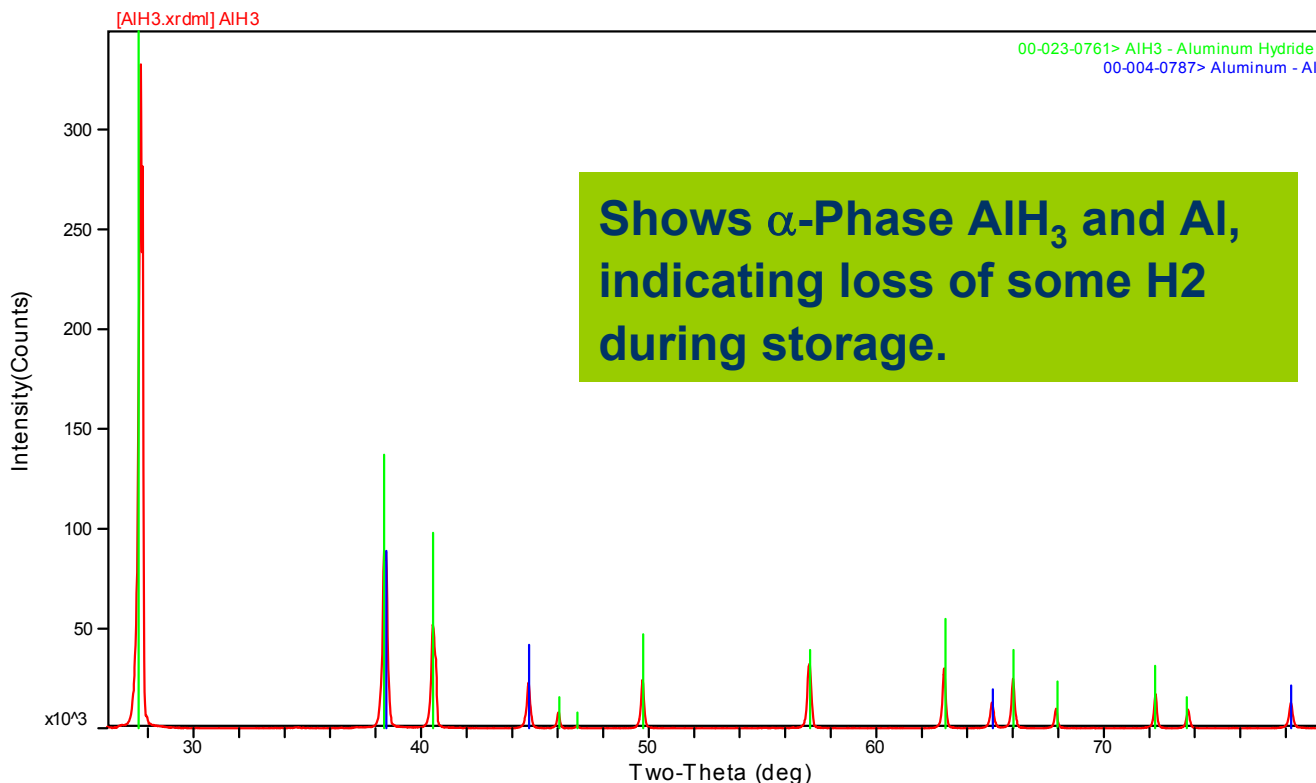
$$C = \sum_i \frac{\delta(E_i - E_m)}{1 + \exp\left(\frac{E_i - \mu}{KT}\right)}$$

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

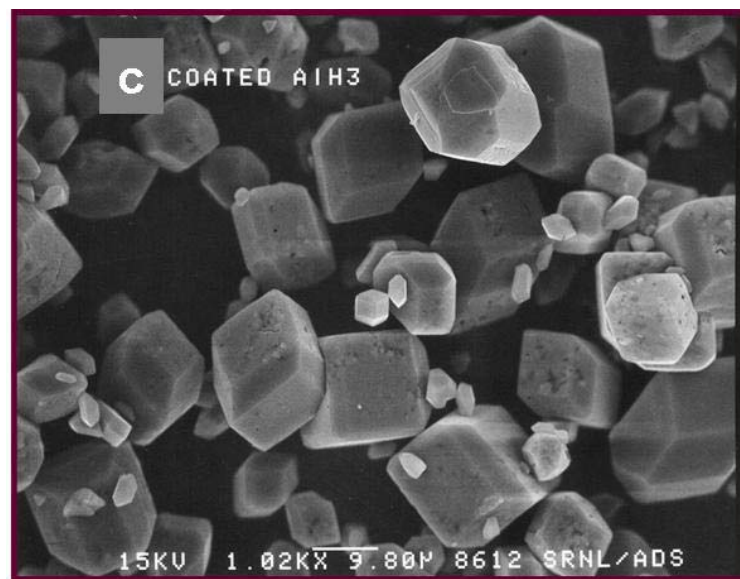
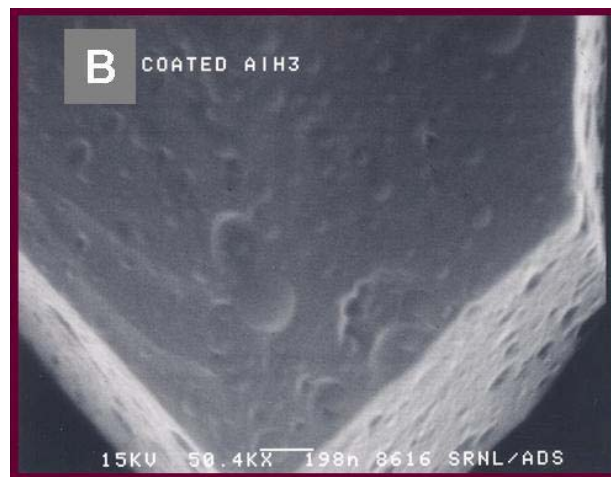
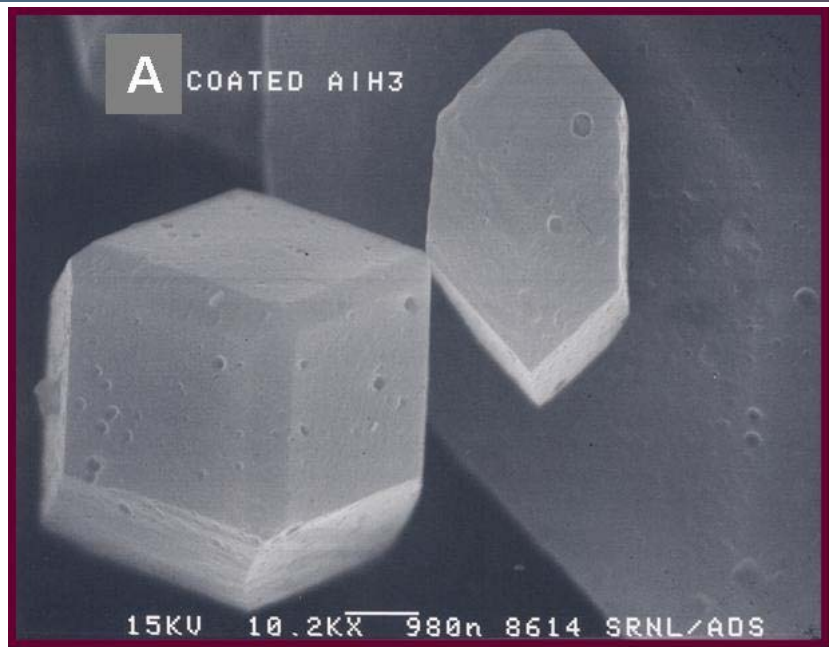
In general

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

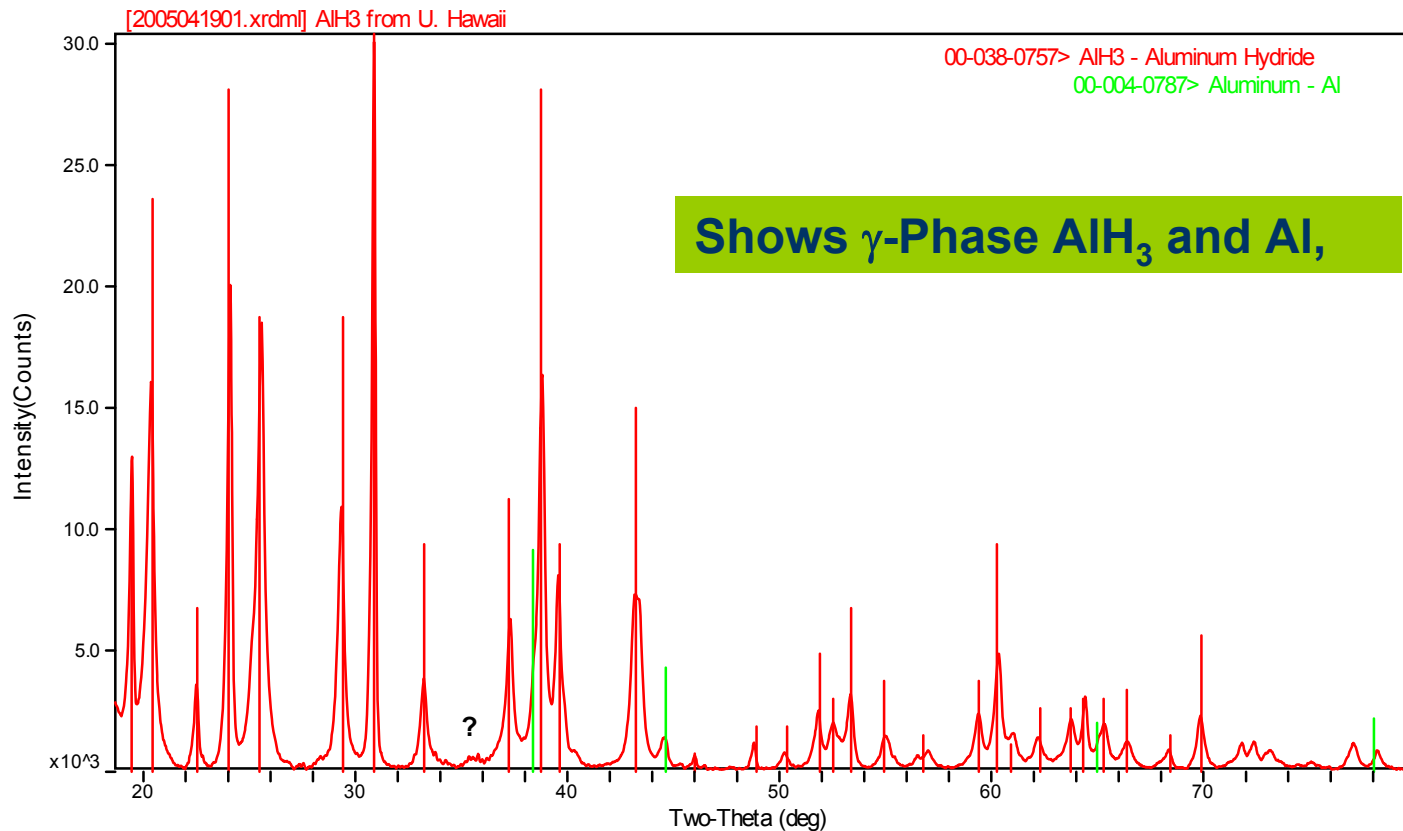
Structure Characterization - XRD



SEM Images of Alane

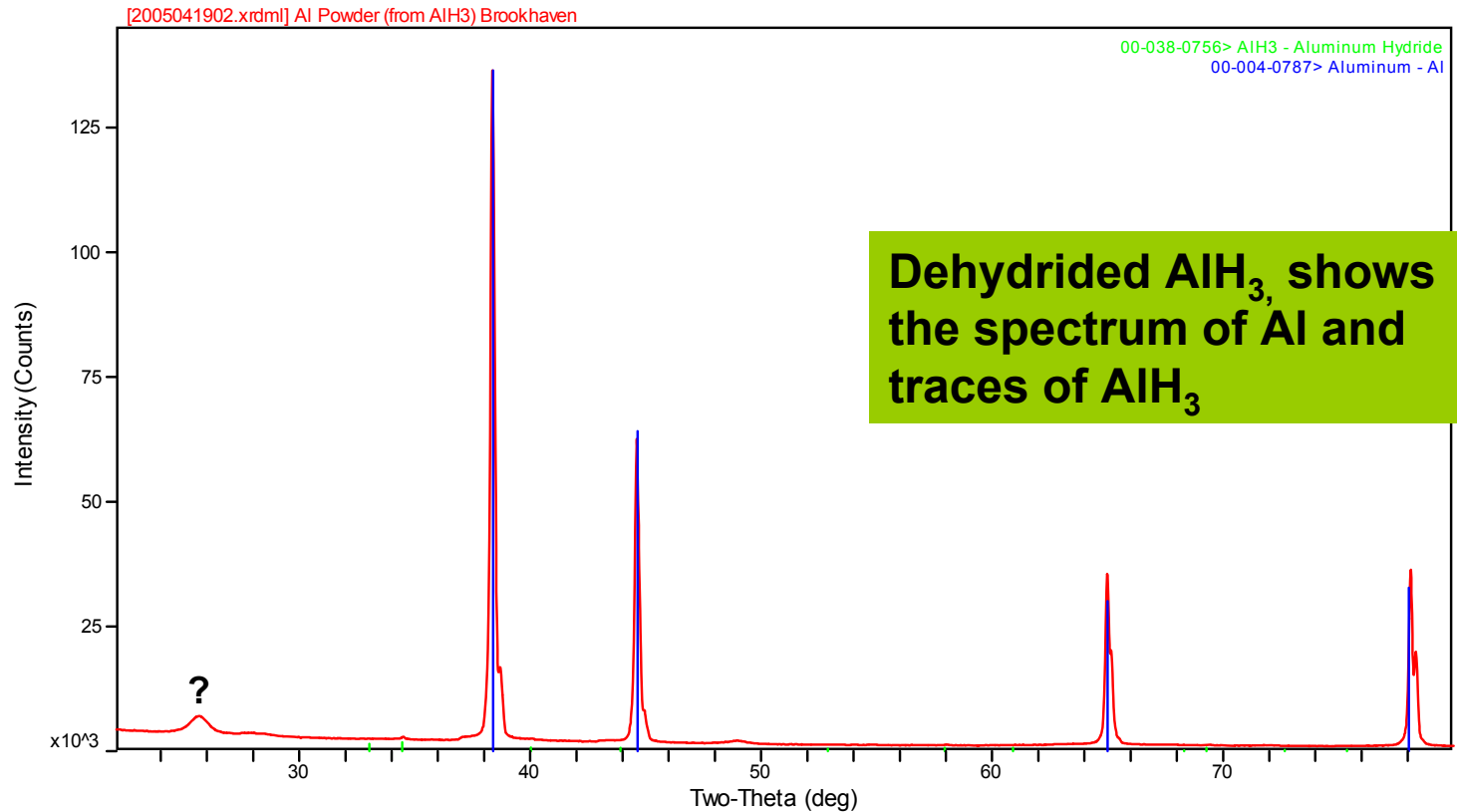


- A. SEM image showing the Crystalline shape of AlH₃
- B. The surface of the crystals shows pitted areas, indicating hydrogen leak
- C. SEM image showing the particle size



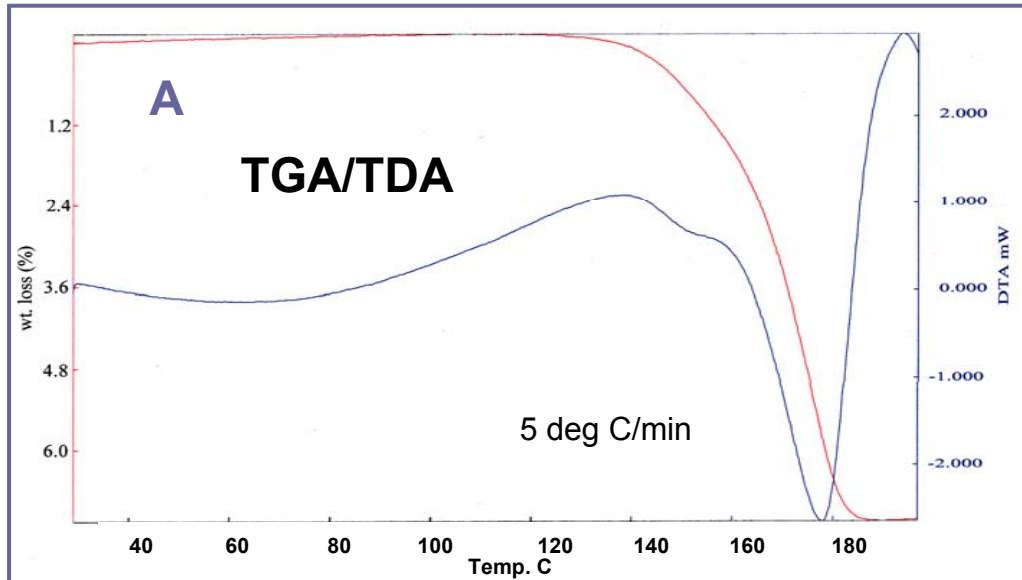
Sample was chemically prepared and provided by
Professor Craig Jensen from University of Hawaii

Structure Characterization - XRD



Sample was provided by Brookhaven National Laboratory (BNL)

Hydrogen Release from Alane



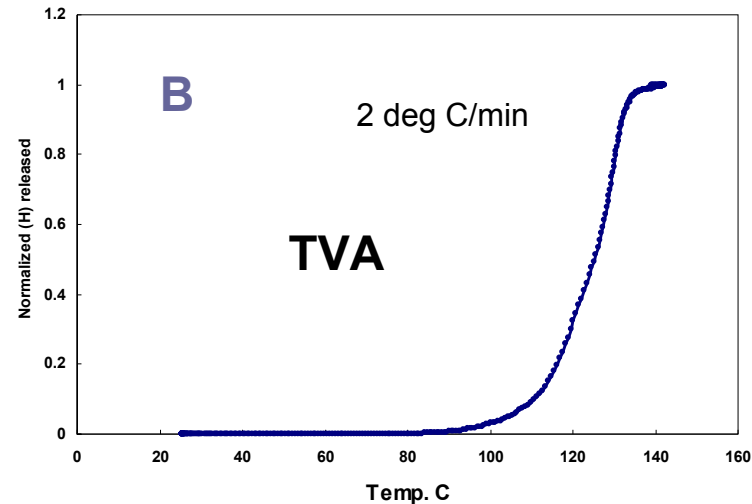
Weight % Released = 7.2 H

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



- **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**

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*