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High-Throughput and Combinatorial Screening of Hydrogen Storage Materials

~Summary of Current Activities at Sandia~

Workshop at Sentech offices, Bethesda, Washington D.C.
June 26, 2007

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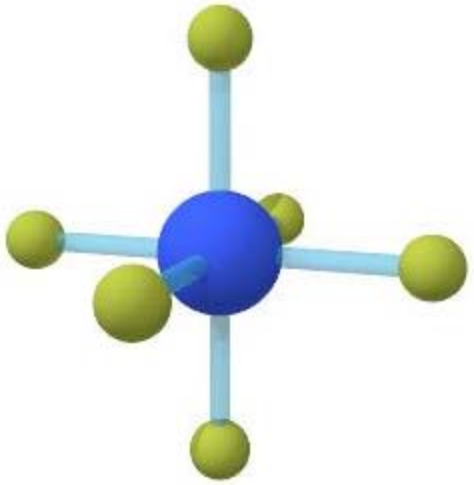
Sandia National Laboratories, CA

Screening for New Metal Hydrides at SNL

- **Select potential high-capacity ternary system and find the cation matrix that stabilizes a certain anionic complex**

- **Theory guidance: Monte Carlo (MC) technique provides minimum energy structures for subsequent enthalpy estimates (E. Majzoub)**

- **Examples of potential structures:**
  - **A-Si-H; A = Li, Na, K, Mg to form $[SiH_x]^{y-}$**
  - **A-Ge-H; A = Li, Na, K, Mg to form $[GeH_x]^{y-}$**
  - **$AB(BH_4)_x$ (mixed borohydrides)**



Anionic complex $[MH_6]^{y-}$

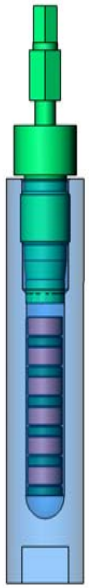
"Traditional" Synthesis Method of Complex Metal Hydrides

"Hot-sintering"

- TM + Binary Hydride (A) + $H_2 \rightarrow A_xTM_yH_z$ (s)
- Hydrogen pressure <100 bar in an autoclave
- Temperature <600°C
- Reaction time: several hours to several days
- Most known complex metal hydrides have been made by hot-sintering, but only a few groups in the world uses this method

The sintering technique is used by groups at: U. Geneva (Switzerland), MPI (Germany), Stockholm University (Sweden), IFE (Norway), SRNL (USA), U. Tohoku, AIST (Japan)

High-pressure Sintering Technique for Screening for New Complex Metal Hydrides



Metal + Binary Hydride + H_2 → Complex Hydride
Boride + Binary Hydride + H_2 → Metal Borohydride

Established a synthesis route that combines high-energy milling (SPEX) followed by hot-sintering under high H_2-pressures (in-house station)

We can test six samples per experiment at a certain P, T and reaction time. Screening involves both searching for new materials and catalysts

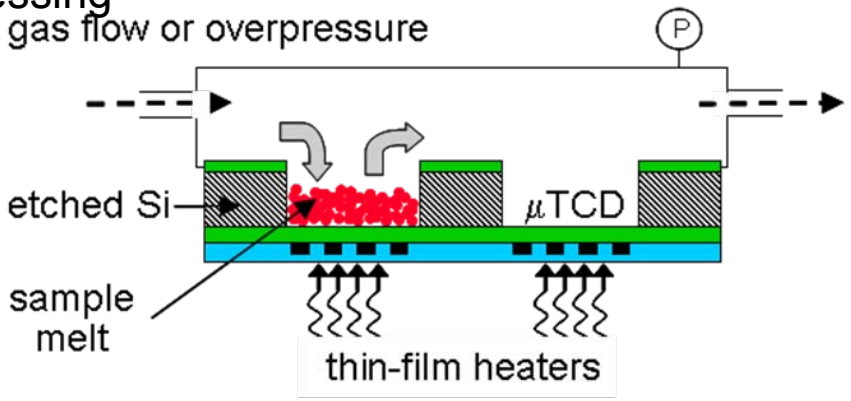
Commercial autoclave with 6 steel crucibles

Normal Run:
<700bar H_2-pressure, <450°C, <48 hours

Our screening technique for new complex anionic materials is competitive with existing high-throughput techniques, but Sandia (McDaniel) is now taking a new approach using multiple micro-hotplates and in-situ diagnostics

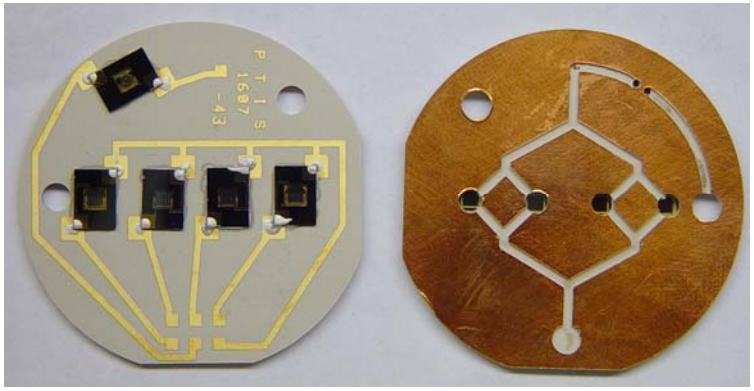
Approach To High Throughput Synthesis And Characterization

- Utilize arrays of micro-hotplates to synthesize and characterize materials
  - High temperature and high pressure processing of precursors
    - *800 °C and 2000 bar H_2*
  - Micro-scale in-situ diagnostics
    - *calorimetry and H_2 gas detection*



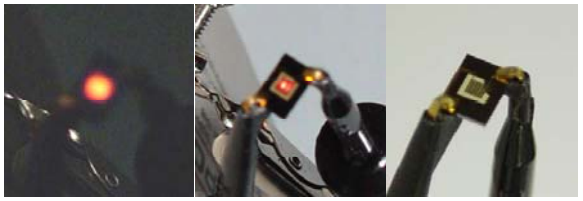
130 bar H_2 fully instrumented prototype

- ✓5 micro-hotplates: 4 samples, 1 H_2 detector
- ✓Calorimeter and gas composition diagnostics (at millimeter length scales)
- ➢Proof Materials: MgH_2, $NaAlH_4$

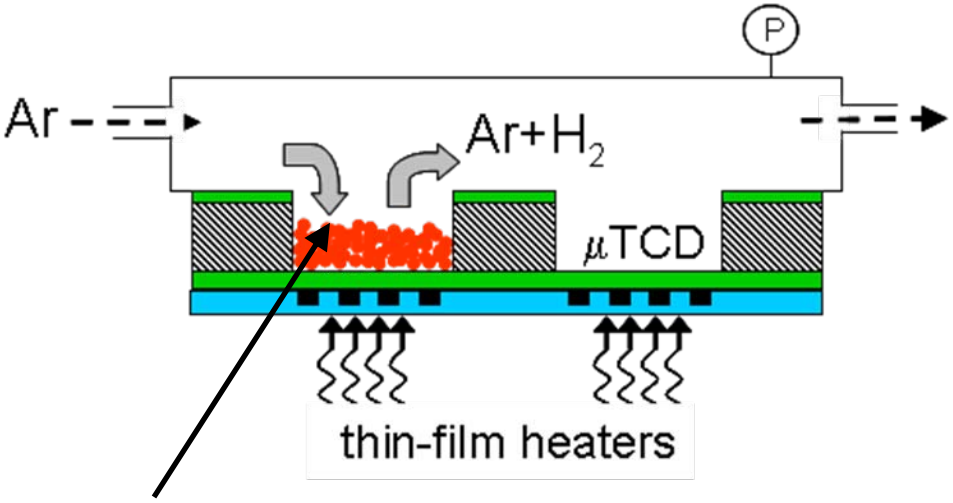


5 micro hot plates with isolated flow channels mount in 2.75” OD flange

hotplate in air at 1000 K

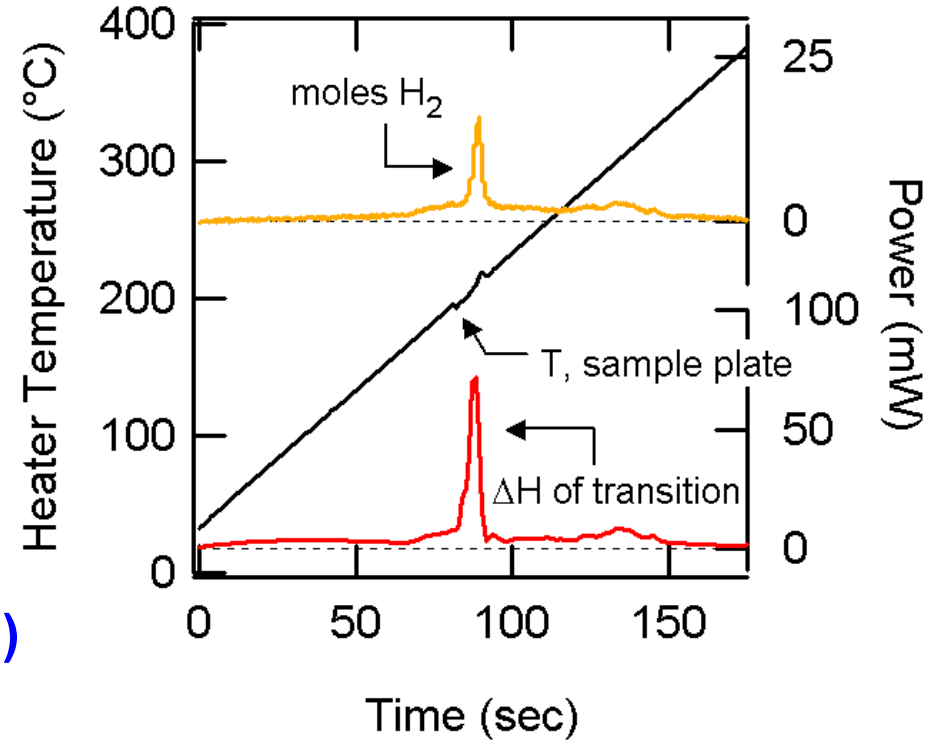


Rapid Characterization With High Sensitivity



(0.1 to 0.5 mg of material)

$NaAlH_4 \rightarrow H_2$ + products

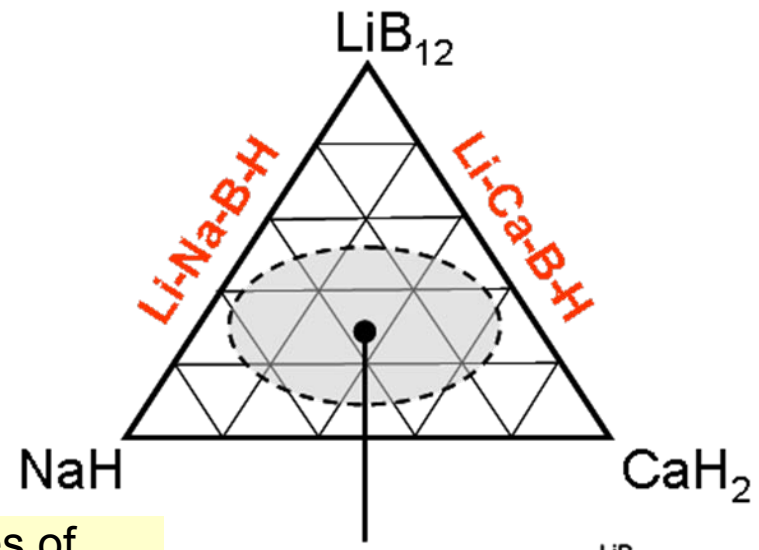


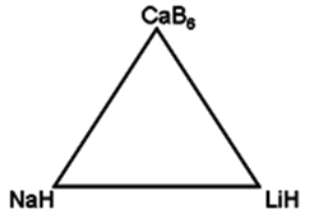
- ✓ **Rapid thermal characterization with high sensitivity**
  - **Transition temperature (kinetics)**
  - **Enthalpy of transition**
  - **H_2 capacity**
- ✓ **Enable a unique combinatorial approach (information rich)!**

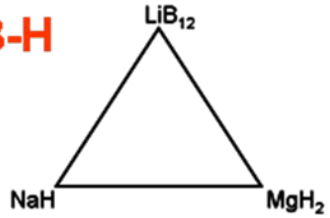
High-throughput Screening Informe By Theoretical Predictions

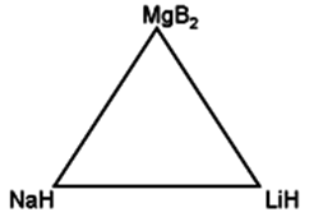
Element	Hydride	Boride
Li	LiH	LiB_2, LiB_{12}
B		
Na	NaH	
Mg	MgH_2	MgB_2
K		
Ca	CaH_2	CaB_6

$xH_2 + yNaH + zLiB_{12} + HEAT \rightarrow$ $Li_2NaB_3H_{12}$, $LiNa_2B_3H_{12}$, $LiNaB_2H_8$, ?





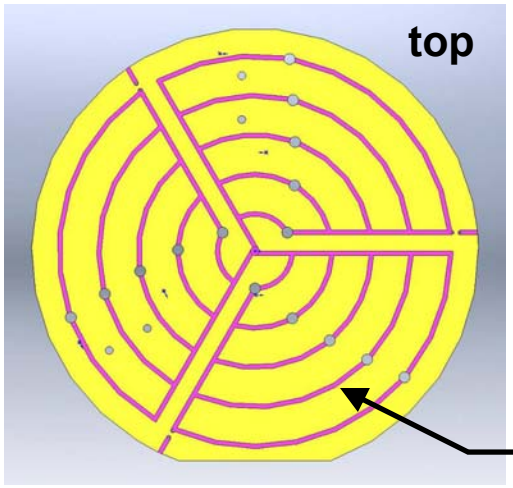


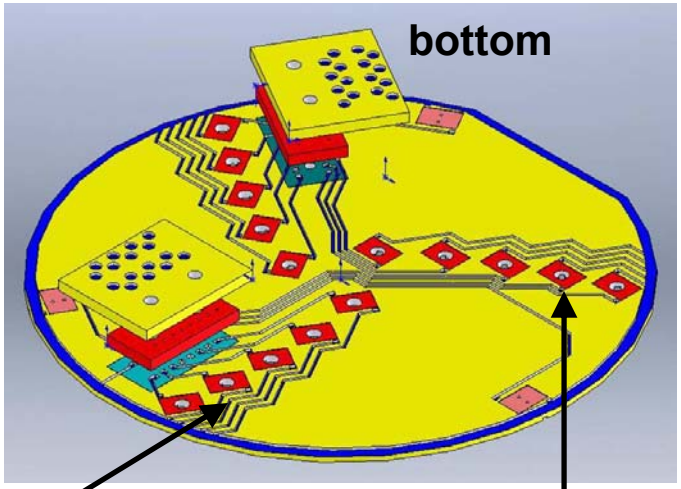


- Statistically based mixing rules of precursor powders determine initial condition
- Survey hydrogen content, transition temperatures and heat fluxes with RTP
- Secondary analysis on promising combinations

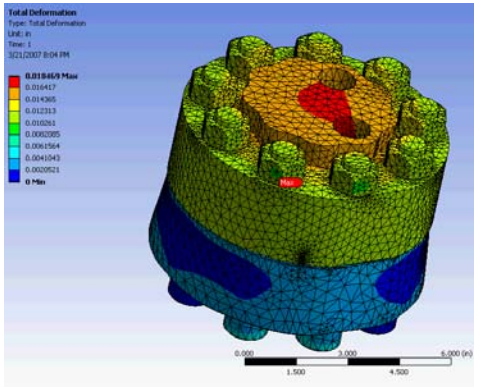
15 Isolated And Fully Multiplexed Sample Wells

multiple micro-hotplates for combinatorial synthesis and characterization





internal flow paths, hotplates, and circuitry mounted on Cu-clad PTFE board



- First generation high pressure vessel design complete
  - 15 sample hotplates, 3 gas detectors
- Achieve sample temperatures of 1200 K and H_2 pressure of 2000 bar
  - Melt or near melt processing from elemental and binary hydride precursors