

# Discovery of H<sub>2</sub> Storage Materials: LiMgN and Mg-Ti-H

Z. Zak Fang and H. Y. Sohn  
University of Utah



Project ID ST062

## Timeline

- Start – March 2005
- Finish – March 2011
- Percent complete – 90%

## Budget

- Total project funding  
DOE share: ~\$950K  
Contractor share: \$240K
- Funding received for FY09: \$280K
- Planned Funding for FY10: \$0K

## Barriers

- Reversible hydrogen content not sufficient (MYPP Barrier A),
- Inadequate kinetic properties (MYPP Barrier B)
- Desorption T's too high (MYPP Barrier B)

## MHCoE Partners

- JPL, CalTech, GE, UNR, U Hawaii, SNL, SRNL, ORNL, U Pitt, CMU, Georgia Tech, Intematix,
- Project Lead: U of Utah

## Objectives and Impact

### Overall

- Discover new solid hydrides that meet reversibility and kinetics requirements
- Develop chemical vapor synthesis process (CVS) for production of nanosized solid metal hydrides
- Demonstrate the effectiveness and unique properties of nanosized solid hydride materials

### FY09-10

- Study thermodynamic properties of hydrogen storage using LiMgN
- Study kinetic properties of hydrogen storage using LiMgN
- Search for catalytic additives that improve kinetics of hydrogen storage using LiMgN
- Study the kinetics of hydrogen storage of high-energy-high-pressure milled  $\text{MgH}_2\text{-}0.1\text{TiH}_2$  system

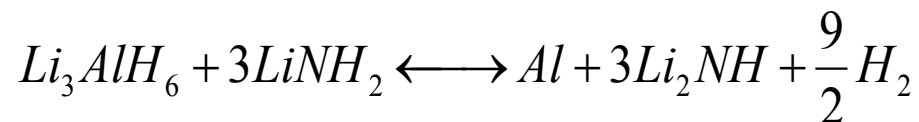
- Exploit potentials of ternary nitrides.
- Use an ultra-high-energy high-pressure milling method and a chemical vapor reaction technique for synthesis of nano particles and study of the effect of nanosize scale ( $\leq 10\text{nm}$ ).
- Discover and identify new candidate materials through collaborations with MHCoe Theory Group.
- Using a two-step strategy for identifying research path among multiple candidate materials:
  - *rapid-screening using in-house tools (e.g. TGA, XRD)*
  - *in-depth study by collaborating with MHCoe partners (NMR, in-situ XRD etc),*
- Implement a criteria based on  $\Delta H$  for select/down-select candidate materials.

## Milestones and Go/No-go Decisions

Month/Year	Milestone or Go/No-Go Decision	Milestone Status
April – 06	Milestone: Complete design and set-up of the chemical vapor synthesis reactor systems and demonstrate their feasibility.	Achieved.
September – 08	A No-Go decision was made on $\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2$ system because the $\Delta H$ of the dehydrogenation reaction is too high ( $\sim 60$ KJ/mol.H <sub>2</sub> )	Completed
March – 2010	Go/No-Go Decision will be made on LiMgN based on comprehensive characterizations of the thermodynamic and kinetic properties of LiMgN with additives.	80% complete
March - 2011	Milestone: Full report, conclusions, and recommendations on selected materials.	On track

## Two promising materials discovered in the past three years:

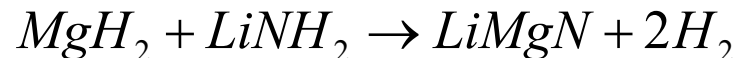
### I. Reactions of $\text{LiNH}_2$ with lithium alanate materials



-- Expected to have theoretical hydrogen capacity in the 6-7 wt% range, coupling known reactions...down-selected due to poor kinetics.

The  $\text{Li}_3\text{AlH}_6/\text{LiNH}_2$  material was “downselected”, removed from further study

### II. Reactions Leading to $\text{LiMgN}$

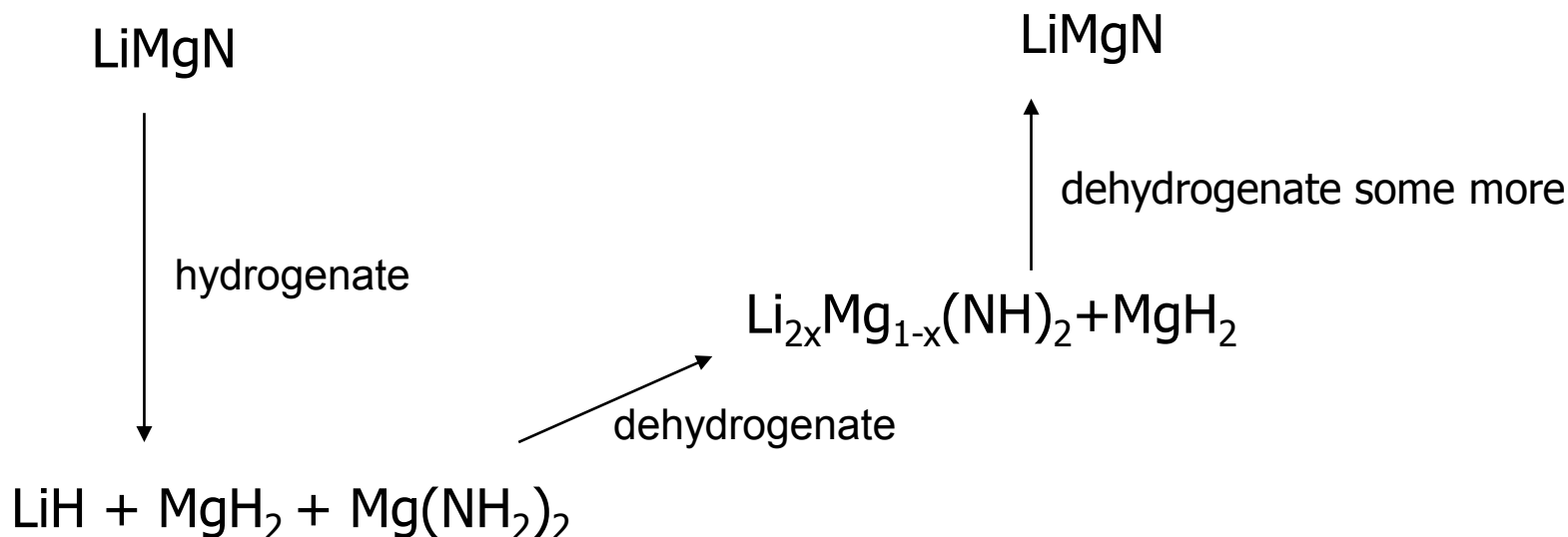


-- Theoretically predicted by MHCoe partners (Johnson, Sholl, Alapati) to have  $\Delta H = 32\text{kJ/molH}_2$ , with 8.2% theoretical hydrogen capacity.

\* Alapati, S.V.; Johnson, K.J., Sholl, D.S. *J.Phys.Chem.*, 2006, 110, 8769

## LiMgN Status at 3/2009 (last annual review)

- ❑ Reactions leading to LiMgN – theoretically predicted by *MHCoE partners* (Johnson, Sholl, Alapati) with 8.2% theoretical hydrogen capacity
- ❑ LiMgN can be hydrogenated at  $T \sim 180$  °C, confirmed by SRNL
- ❑ In-situ XRD studies (GE) of hydrogenation/dehydrogenation indicate overall reaction scheme:

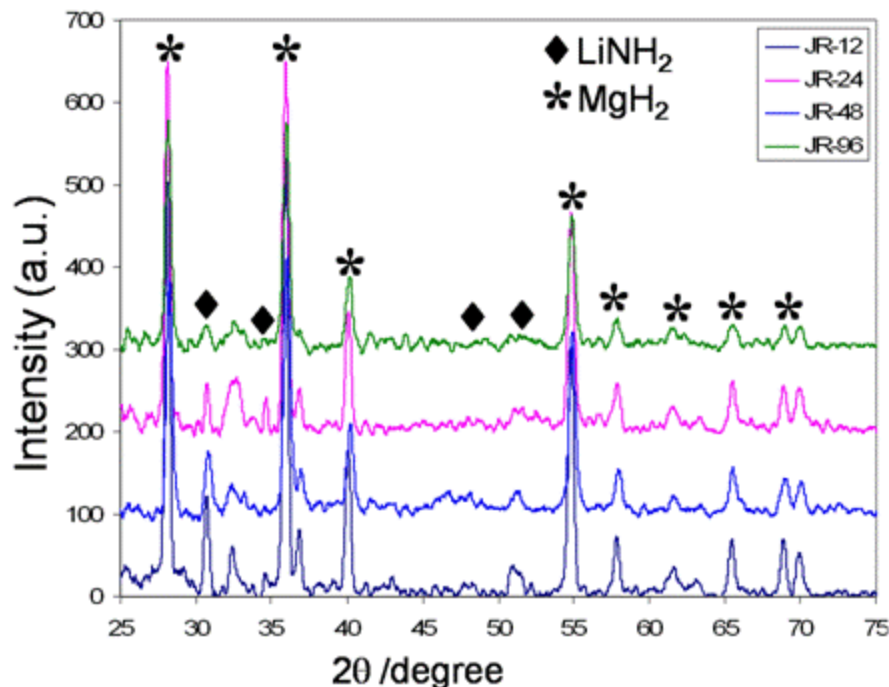


## Recent results on LiMgN

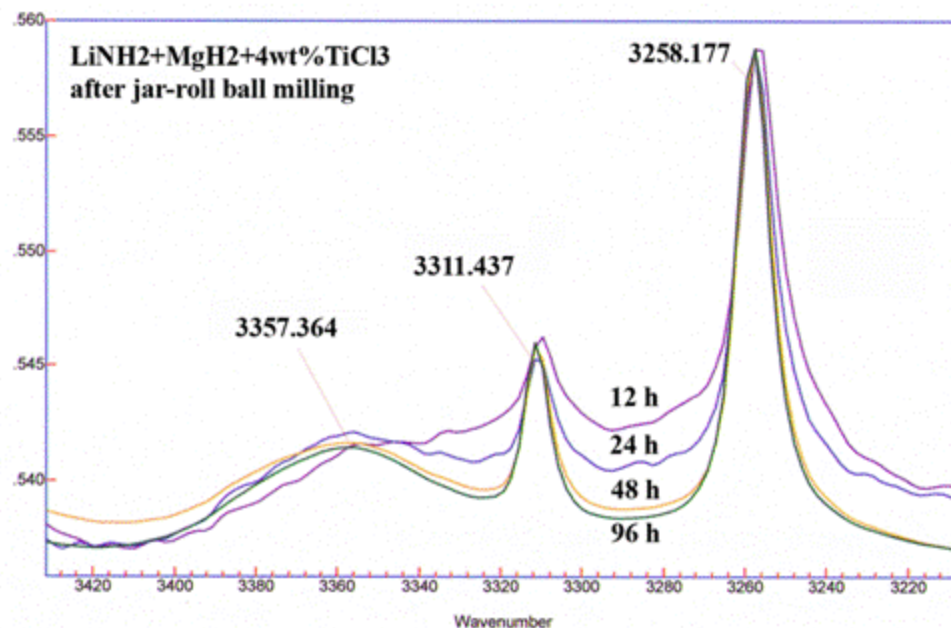
- I. Preparation of LiMgN from the  $\text{LiNH}_2 + \text{MgH}_2$  reaction
- II. PCT study of hydrogenation and dehydrogenation using LiMgN as starting material



## Effects of ball milling intensity on the synthesis of pure LiMgN



XRD patterns of LiNH<sub>2</sub>/MgH<sub>2</sub> mixture after Jar-roll milling



FT-IR Spectra of LiNH<sub>2</sub>/MgH<sub>2</sub> mixture after Jar-roll milling

*Low-energy milling using a jar-rolling set-up preserves the LiNH<sub>2</sub>/MgH<sub>2</sub> mixture, without premature release of H<sub>2</sub>*

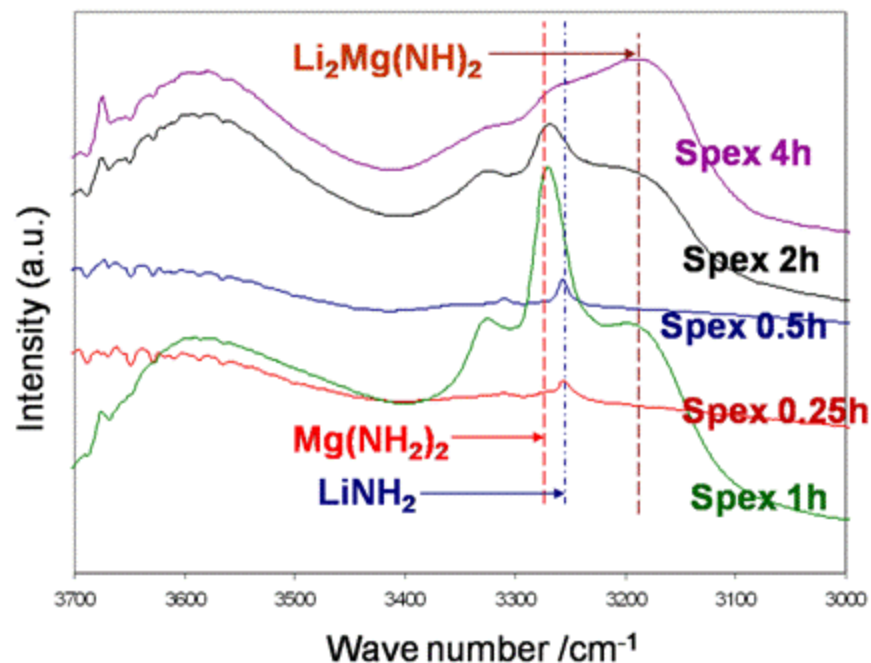
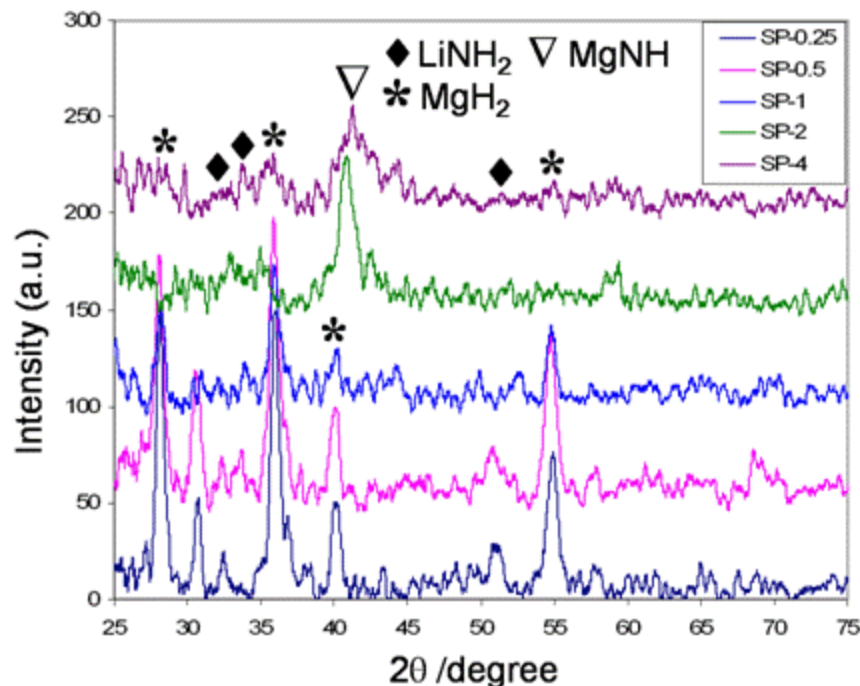
## *Effects of ball milling intensity on the synthesis of pure LiMgN*

### Summary of the mixture of LiNH<sub>2</sub>/MgH<sub>2</sub> after Jar-roll milling

Low-energy mill	12 hrs	24 hrs	48 hrs	96 hrs
TGA (wt.%)	9.19	8.02	7.87	7.91
XRD after milling	MgH <sub>2</sub> , LiNH <sub>2</sub>	MgH <sub>2</sub> , LiNH <sub>2</sub>	MgH <sub>2</sub> , LiNH <sub>2</sub>	MgH <sub>2</sub> , LiNH <sub>2</sub>
FT-IR after milling	LiNH <sub>2</sub>	LiNH <sub>2</sub>	LiNH <sub>2</sub>	LiNH <sub>2</sub>
XRD after dehydrogenation	LiMgN, Li <sub>3</sub> N	LiMgN, Li <sub>3</sub> N	LiMgN, Mg <sub>3</sub> N <sub>2</sub>	LiMgN

*After low-energy milling, reactions during subsequent heating produce pure (98.99%) LiMgN from the sample after longer milling time (>48h)*

## Effects of ball milling intensity on the synthesis of pure LiMgN



XRD patterns of LiNH<sub>2</sub>/MgH<sub>2</sub> mixture after Spex milling

FT-IR Spectra of LiNH<sub>2</sub>/MgH<sub>2</sub> mixture after Spex milling

*High-energy milling leading to a series of reactions during the milling process, including the reactions between LiNH<sub>2</sub> and MgH<sub>2</sub>, and the subsequent release of hydrogen.*

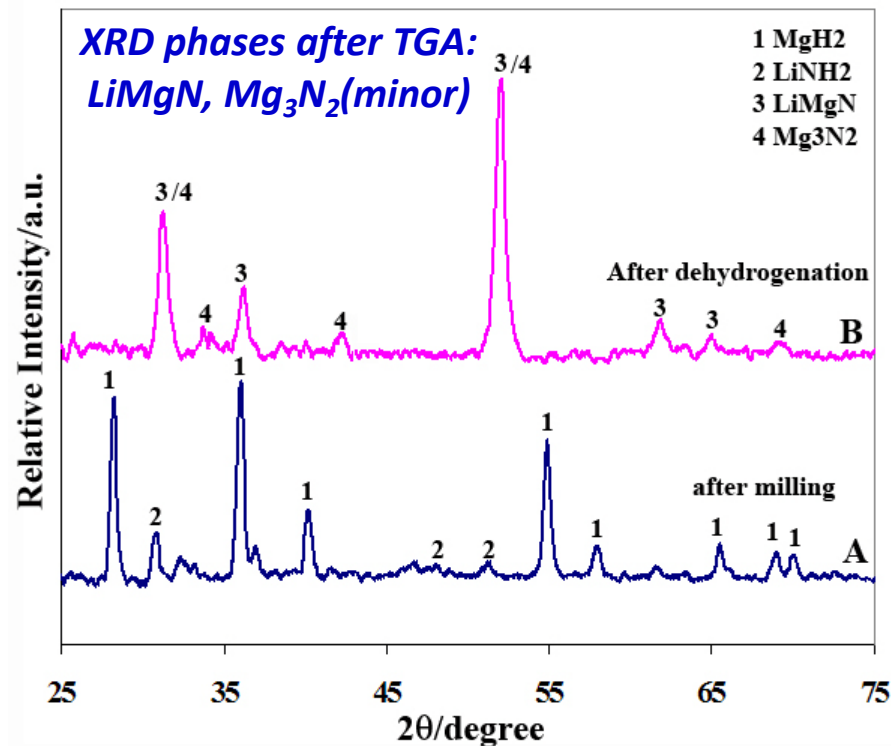
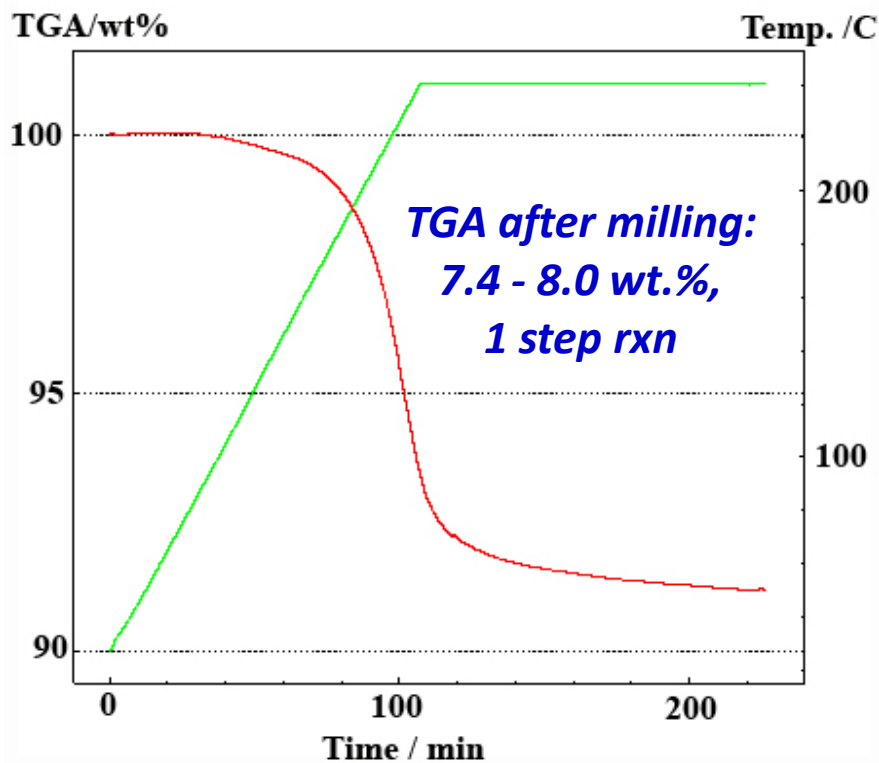
## *Effects of ball milling intensity on the synthesis of pure LiMgN*

### Summary of the mixture of LiNH<sub>2</sub>/MgH<sub>2</sub> after Spex milling

High-energy mill	0.25 hr	0.5 hr	1 hr	2 hrs	4 hrs
TGA wt. %	9.124	8.192	5.723	4.511	3.422
XRD after milling	LiNH <sub>2</sub> , MgH <sub>2</sub>	LiNH <sub>2</sub> , MgH <sub>2</sub>	MgH <sub>2</sub>	MgNH	MgNH
FT-IR after milling	LiNH <sub>2</sub>	LiNH <sub>2</sub>	Mg(NH <sub>2</sub> ) <sub>2</sub> , Li <sub>2</sub> Mg(NH) <sub>2</sub> , MgNH	Mg(NH <sub>2</sub> ) <sub>2</sub> , Li <sub>2</sub> Mg(NH) <sub>2</sub> , MgNH	Li <sub>2</sub> Mg(NH) <sub>2</sub> , MgNH
XRD after dehydrogenation	LiMgN, Mg <sub>3</sub> N <sub>2</sub>	LiMgN, Mg <sub>3</sub> N <sub>2</sub>	LiMgN, Mg <sub>3</sub> N <sub>2</sub>	LiMgN, Mg <sub>3</sub> N <sub>2</sub> ,	LiMgN, Mg <sub>3</sub> N <sub>2</sub> ,

*The product after high milling is a complex mixture of multiple phases. Pure LiMgN cannot be obtained from High-energy method*

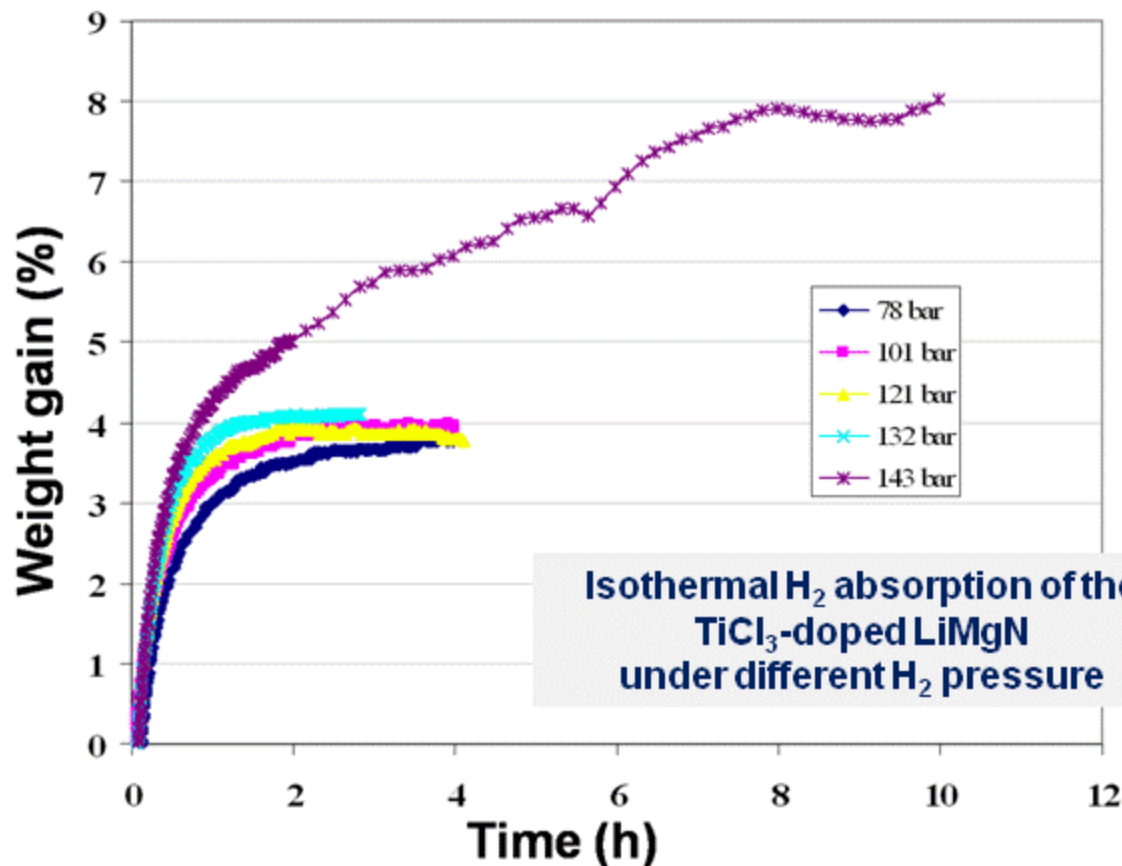
## Effects of ball milling intensity on the synthesis of pure LiMgN



### Optimum milling procedures:

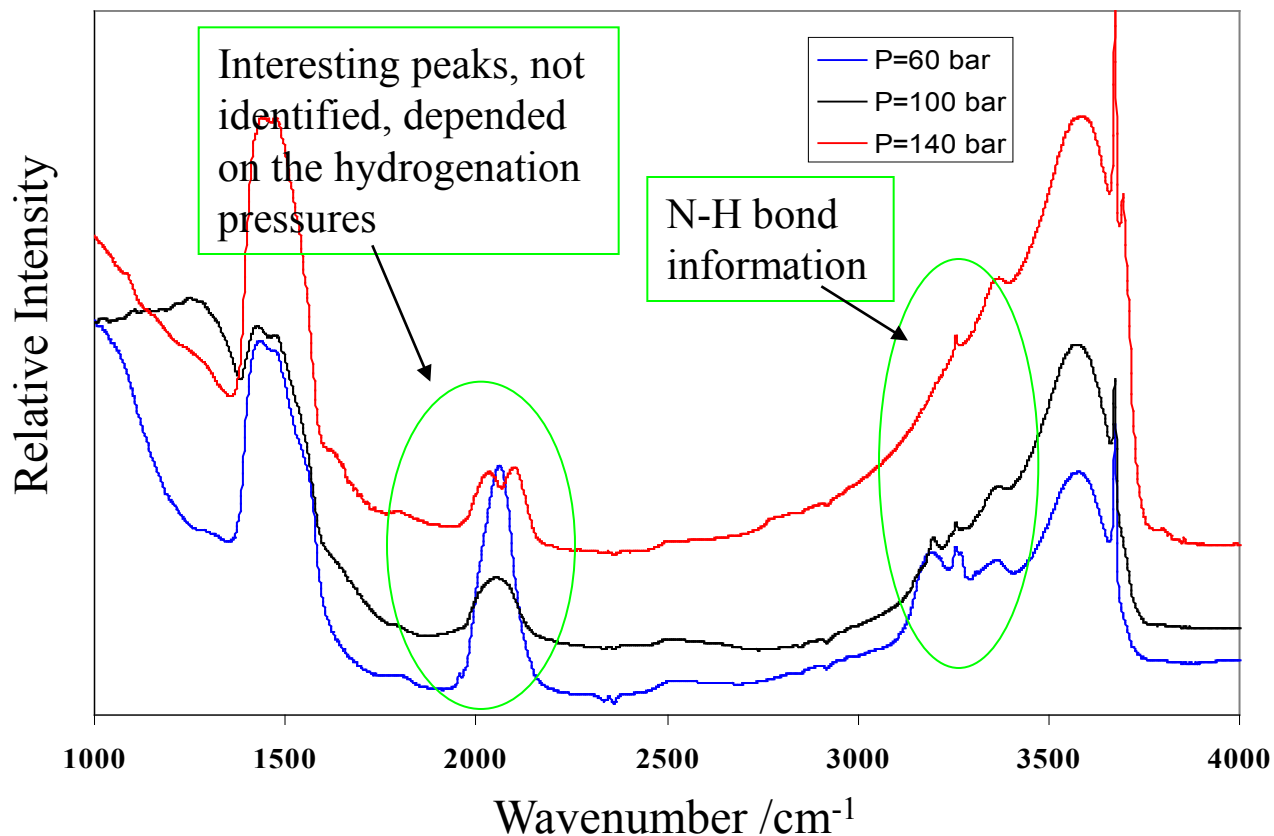
- 1). Spex milling separately (LiNH<sub>2</sub> & MgH<sub>2</sub>/TiCl<sub>3</sub>)(4h) +
- 2). Jar-roll milling together (LiNH<sub>2</sub>+MgH<sub>2</sub>+TiCl<sub>3</sub>)(96h)
- 3). Dehydrogenation at 260°C with 2°C/min for 4h

## Hydrogenation of LiMgN by PCT



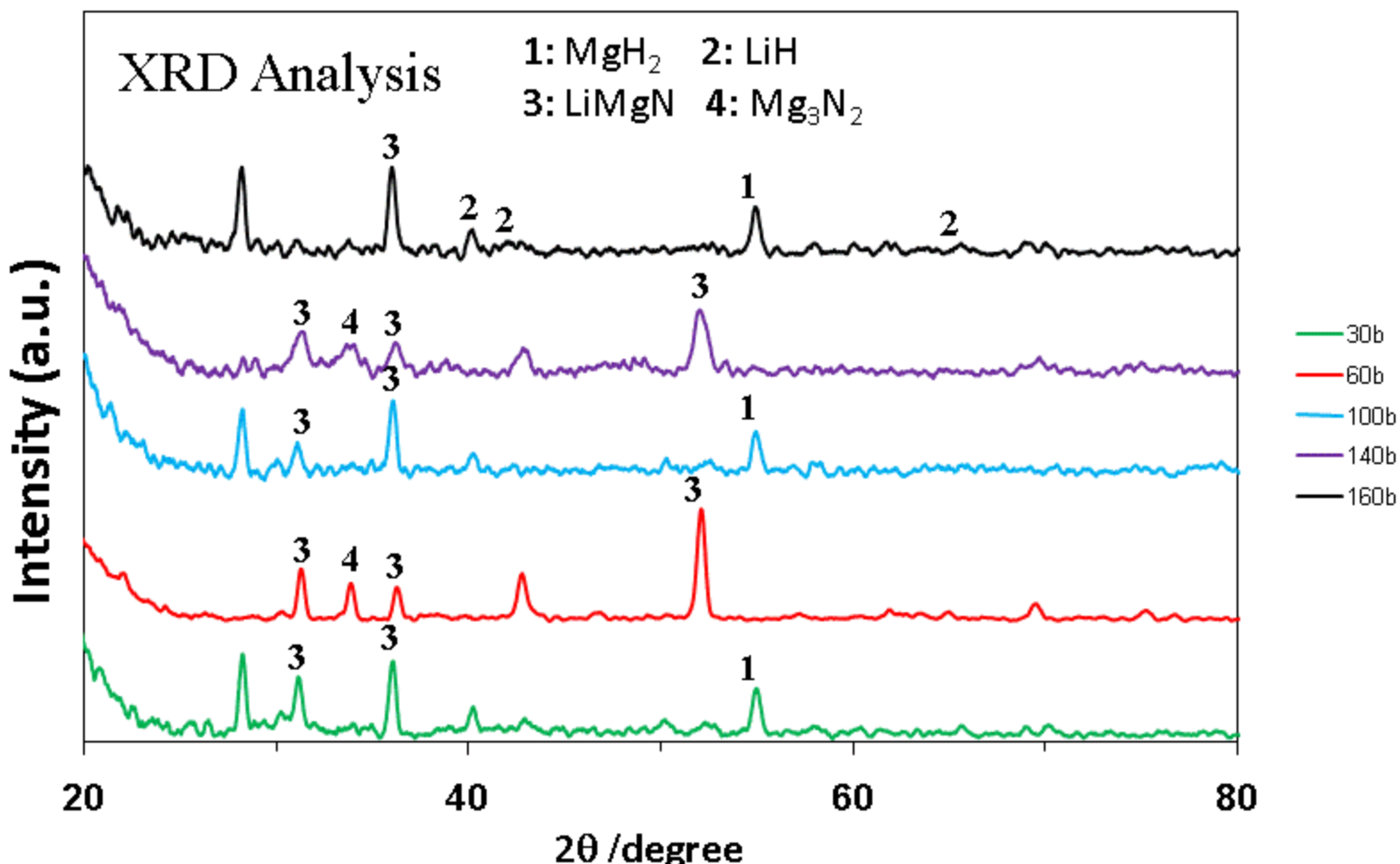
- Hydrogenation of LiMgN is pressure sensitive
- >140 bar is required for full recharging

## Hydrogenation of LiMgN by PCT



FTIR spectrum analysis consistent w/ TGA and XRD data.

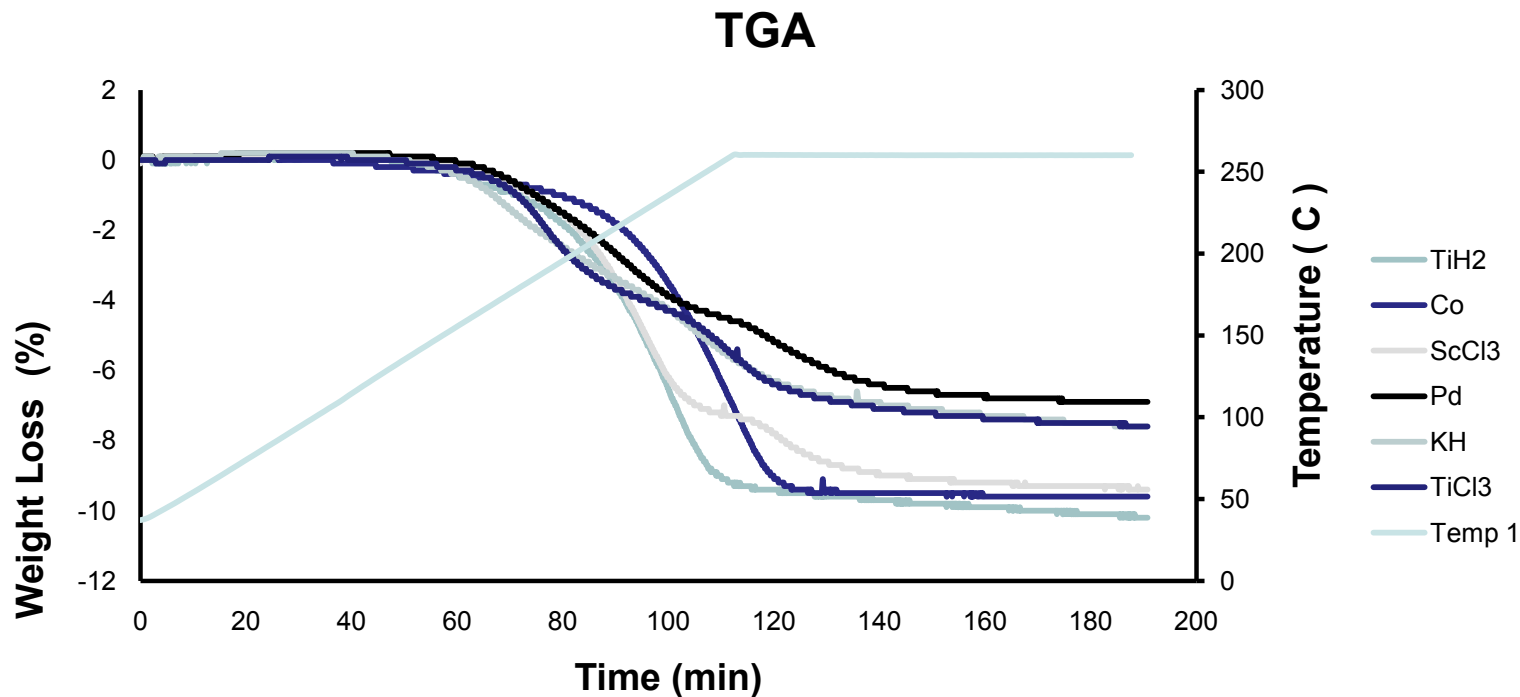
## Hydrogenation of LiMgN by PCT



XRD data consistent with TGA and XRD data.



## Search for catalysts for LiMgN



A series of catalytic additives affect the kinetics of  $\text{LiNH}_2 + \text{MgH}_2$  reactions.

## Search for catalysts for LiMgN

Catalyst Formula	Weight Loss (%)	Onset temperature	Onset Time (min)	Time needed for 90% conversion
TiH <sub>2</sub>	6.9	104	38	~ 20
Co	9	76	24	~ 25
ScCl <sub>3</sub>	9.6	93	33	~ 17
Pd	7.3	98	35	~ 22
KH (50% Paraffin)	7.9	80	30	~ 23
TiCl <sub>3</sub>	6.2	110	40	~ 17

A series of catalytic additives affect the kinetics of LiNH<sub>2</sub>+MgH<sub>2</sub> reactions.

## Summary of Ternary Nitride LiMgN:

- Reversible,
- Reversible capacity 6-8wt%
- Thermodynamics:  $\Delta H = 33-38 \text{ KJ/mol.H}_2$ ,
- Kinetics – Reasonable at 280 °C.
- NH<sub>3</sub> issue: ~14 ppm in H<sub>2</sub> stream, Cumulative ~100 ppm.
- *First plateau pressure is very low ( $\ll 1$  bar) reducing usable wt%.*
- *Must reduce the reaction temperature. Efforts underway to use additives and nano engineering.*

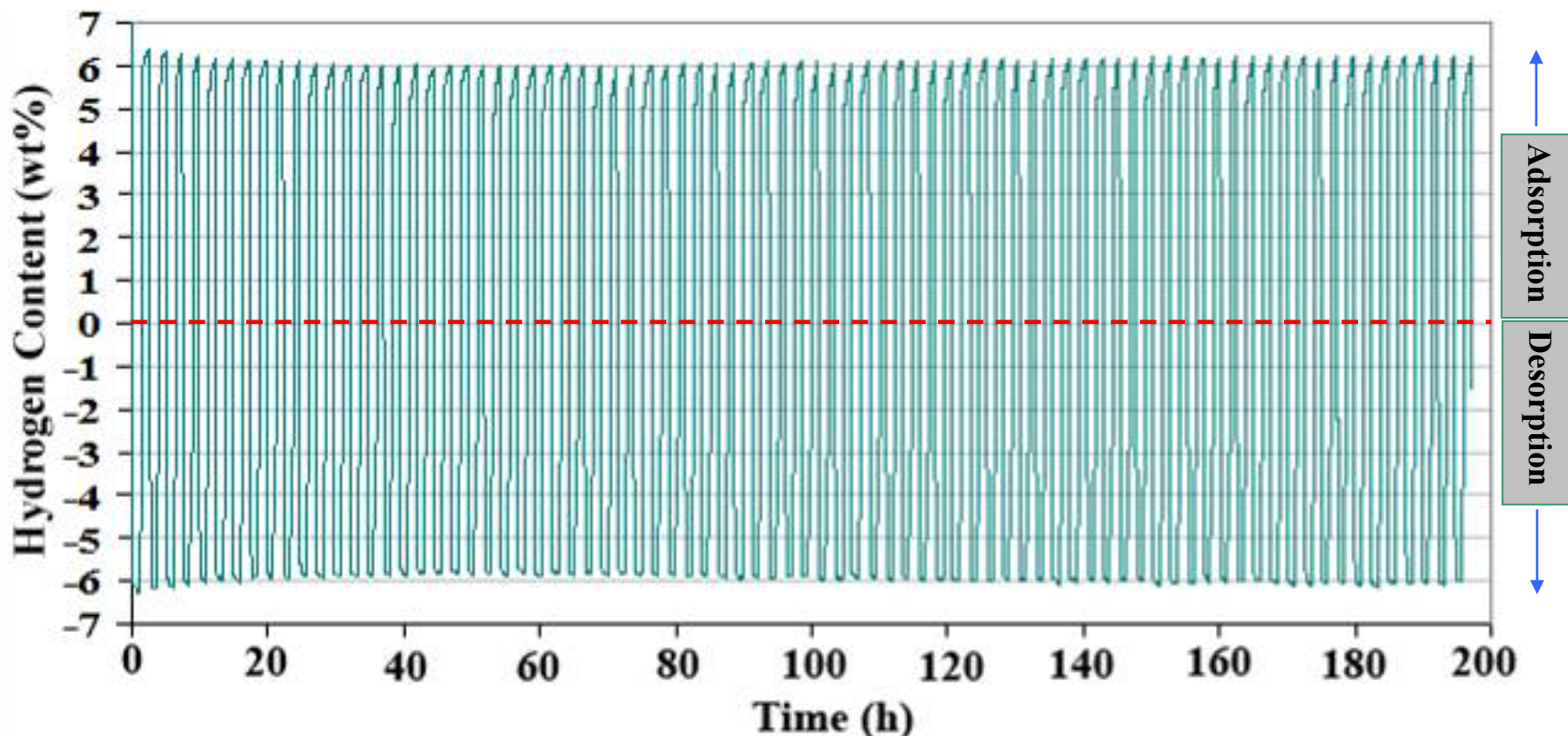
## Non-equilibrium Mg-Ti-H Material System

- Non-equilibrium Mg-Ti thin film systems have been demonstrated to have significant reversible hydrogen storage capacities<sup>1,2</sup>.
- Can thin film material be replicated in powder or bulk form?
- Hydrogen storage of nano-sized  $\text{MgH}_2$  with  $\text{TiH}_2$  additives, synthesized by high energy high pressure ball milling process was studied.

<sup>1</sup> P. Vermeulen, R.A.H. Niessen, P.H.L. Notten, “Hydrogen storage in metastable  $\text{Mg}_y\text{Ti}(1-y)$  thin films”, *Electrochem. Commun.* 8 (2006) 27-32.

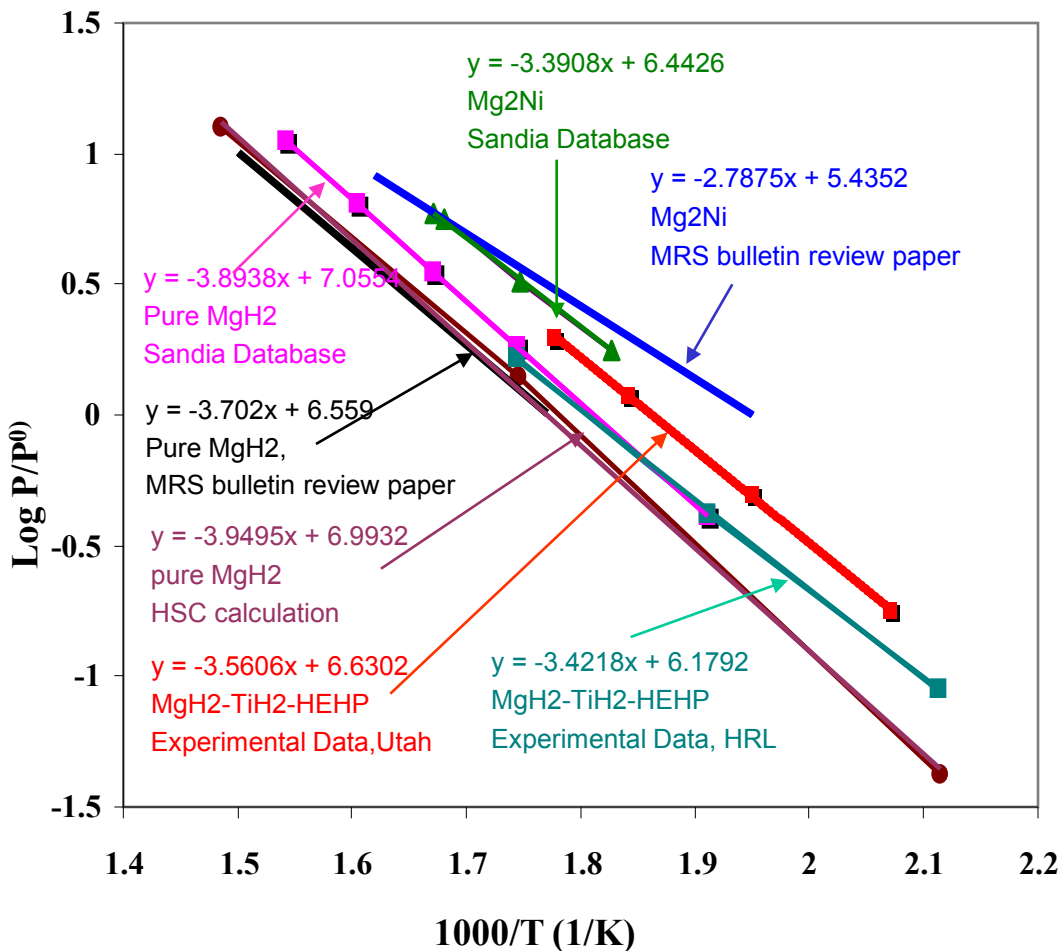
<sup>2</sup>. B. Clemens et al. MHCoe internal communication.

## Hydrogen Storage of nano sized scale: $\text{MgH}_2$ -8mol% $\text{TiH}_2$ , particle size – 5-10 nm



Excellent stability after 100 cycles at 290 °C. ~6.0 wt% reversible capacity.

## Hydrogen Storage of nano sized scale: $MgH_2$ -8mol% $TiH_2$ , particle size – 5-10 nm

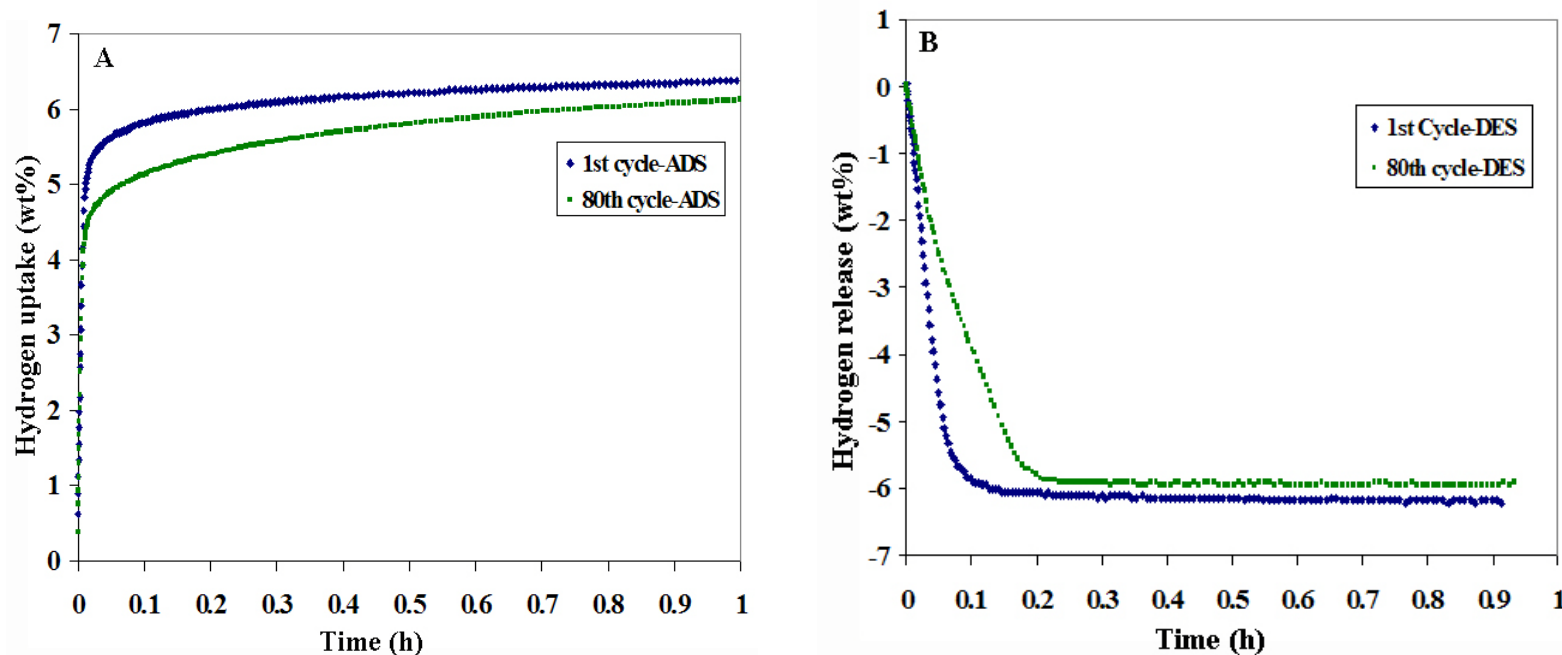


System	$\Delta H$ (kJ/K mol $H_2$ )	$\Delta S$ (J/mol $H_2$ )
Pure $MgH_2$ , (Sandia Database)	-74.6	-135.1
Pure $MgH_2$ , (MRS Bull. Sept. 2002)	-70.8	-125.6
Pure $MgH_2$ , (HSC calculation)	-75.6	-133.9
$MgH_2-TiH_2-HEHP$ (Exp. Data, U Utah)	-68.2	-126.9
$MgH_2-TiH_2-HEHP$ (Exp. Data, HRL)	-65.5	-118.3
$Mg_2Ni$ , (Sandia Database)	-64.9	-123.4
$Mg_2Ni$ , (MRS Bull. Sept. 2002)	-53.4	-104.1

Using nano size (5-10 nm) and  $TiH_2$  additives, the  $\Delta H$  value was changed, but so was  $\Delta S$ . The net effect on  $\Delta G$  very small. Thus,  $P_{eq}$  did not change significantly.

## Hydrogen Storage of nano sized scale: $\text{MgH}_2\text{-8mol\%TiH}_2$

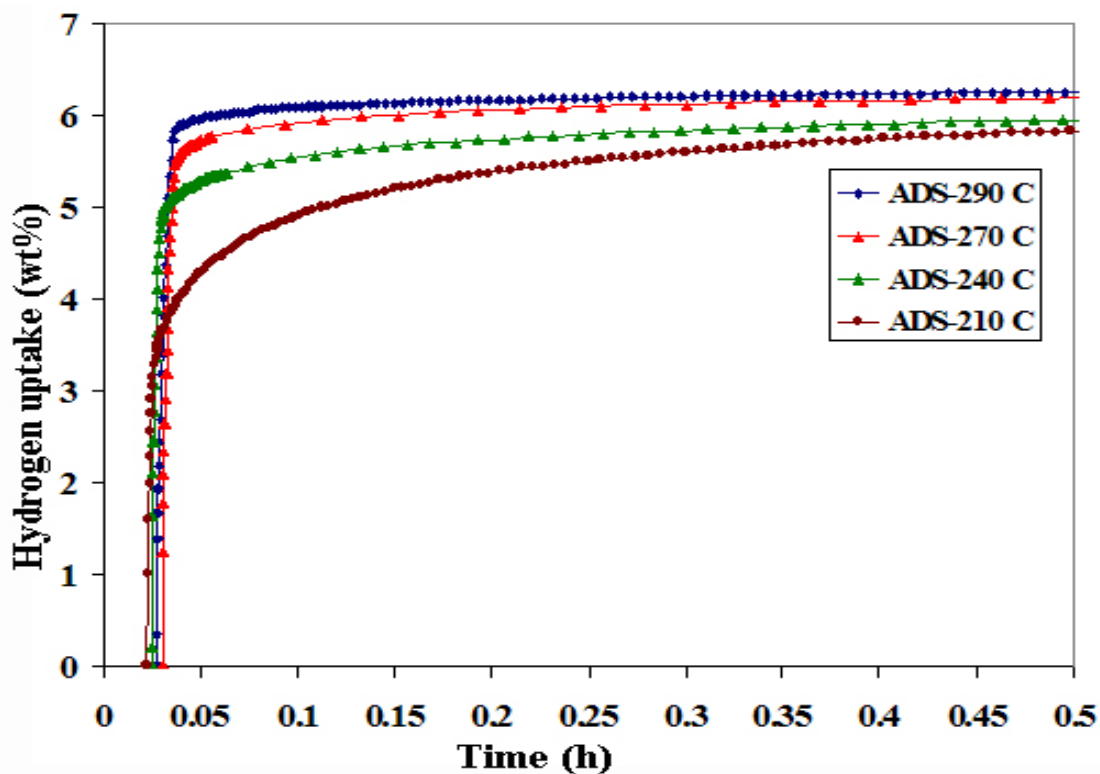
### Comparison of hydrogen uptake and release at the 1<sup>st</sup> and 80<sup>th</sup> cycle



A) Isothermal dehydrogenation of the milled  $\text{MgH}_2/0.1\text{TiH}_2$  under 1kPa hydrogen pressure at 300 °C during the 1st and 80th cyclic kinetics measurements, respectively; B) Isothermal hydrogenation of the dehydrogenated  $\text{MgH}_2/0.1\text{TiH}_2$  under 2 MPa hydrogen pressure at 300 °C during the 1st and 80th cyclic measurements, respectively.

## Hydrogen Storage of nano sized scale: $MgH_2$ -8mol% $TiH_2$

Hydrogenation rate is high when the temperature is  $>210^\circ C$

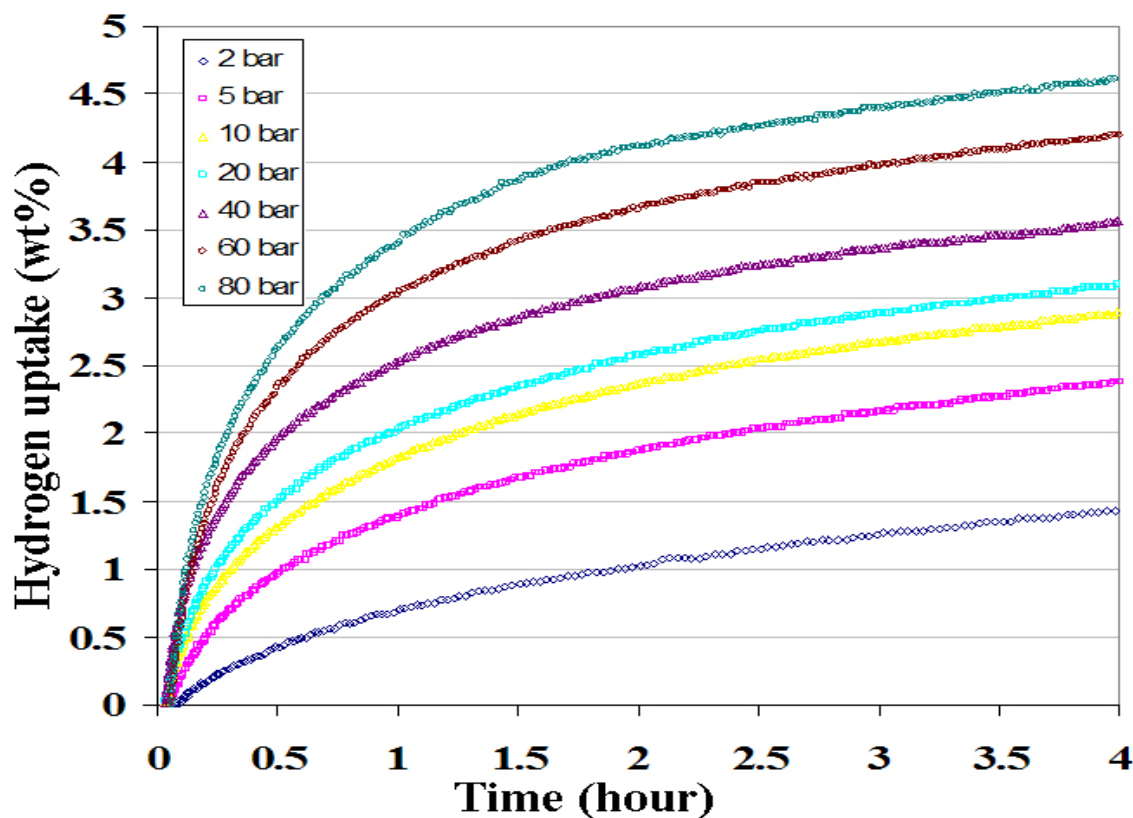


Isothermal hydrogenation of the milled Mg-Ti-H under 2MPa  $H_2$  pressure at 210, 240, 270 and 290  $^\circ C$ , respectively.



## Hydrogen Storage of nano sized scale: $MgH_2$ -8mol% $TiH_2$ , particle size – 5-10 nm

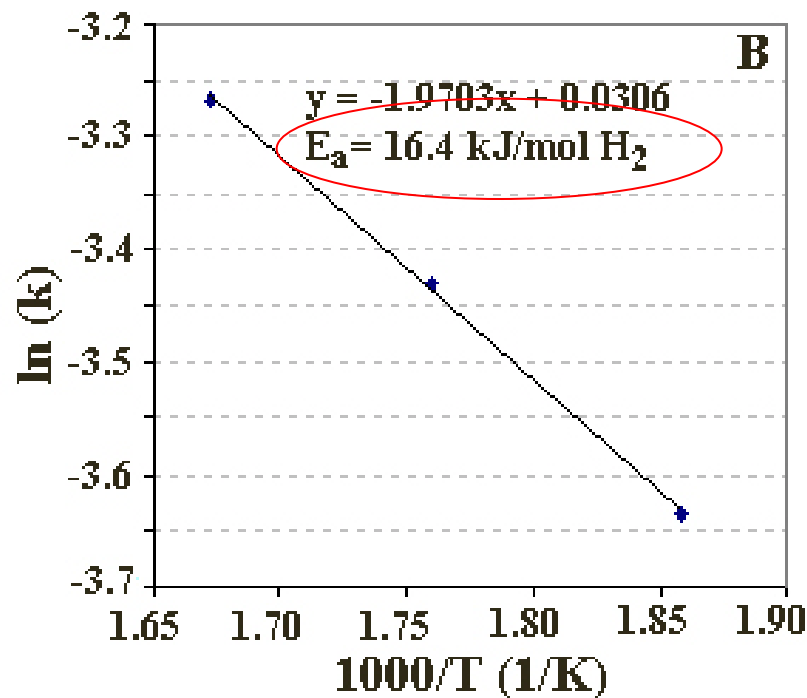
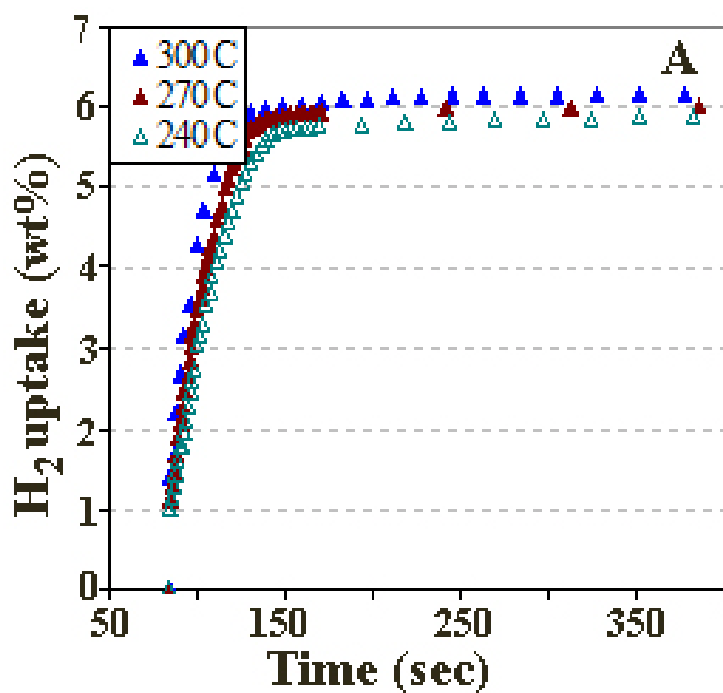
Significant  $H_2$  uptake by Mg at room temperature



*Isothermal hydrogenation profiles of the Mg-Ti-H system at room temperature.*

## Hydrogen Storage of nano sized scale: MgH<sub>2</sub>-8mol%TiH<sub>2</sub>

### Activation for Hydrogenation Reaction

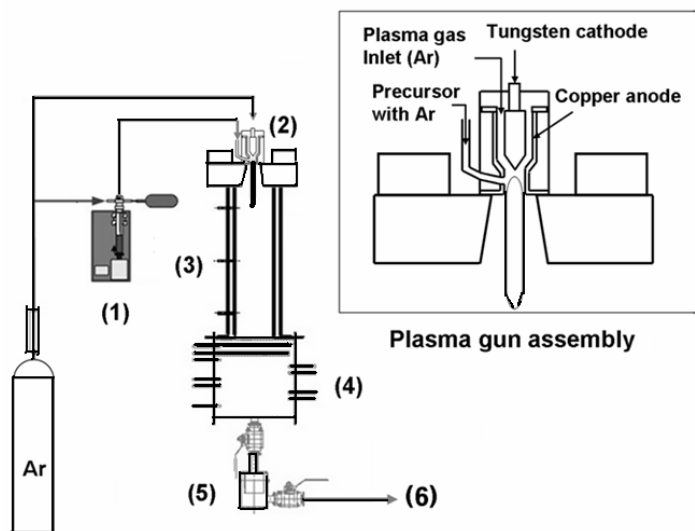


$$E_a = -RT \ln(k/k_0) \quad (1)$$

$$d\alpha/dt = k \cdot f(\alpha) \quad (2)$$

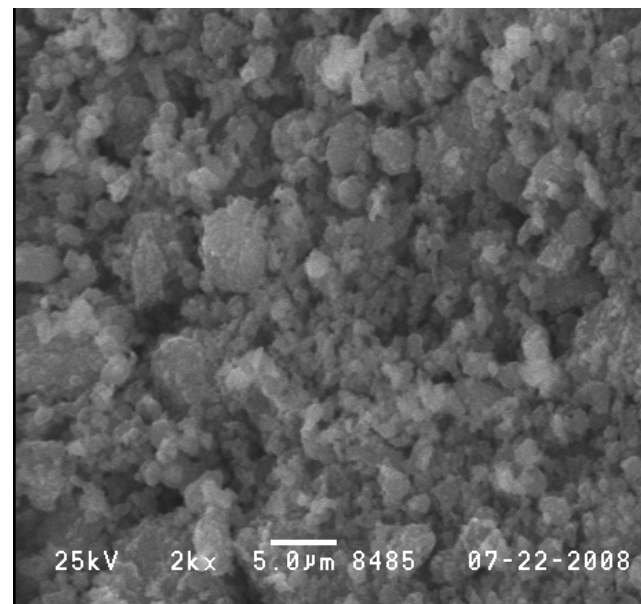
$$kt = -\ln(1-\alpha) \quad (3)$$

## Synthesis of Ti-doped Mg nanopowder by a thermal plasma process



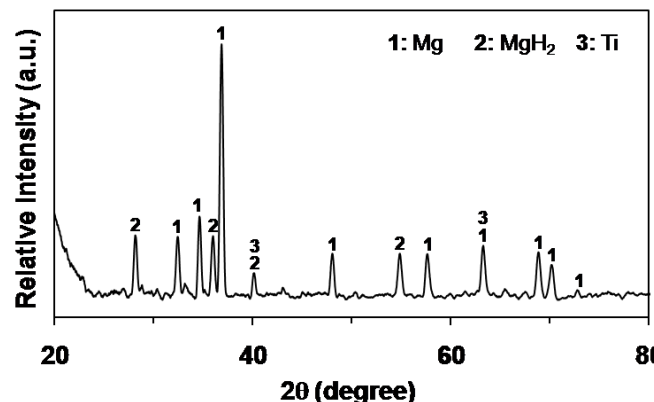
**Schematic diagram of the plasma reactor system**

- (1) entrained-flow powder feeder for precursors ( $MgH_2+TiCl_3$ )
- (2) plasma gun, (3) cylindrical reactor, (4) cooling chamber,
- (5) powder collector, (6) offgas exhaust system.

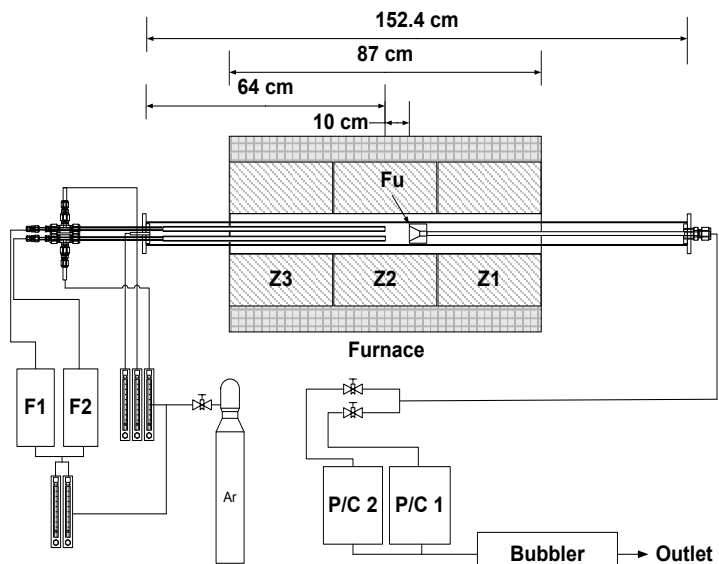


**SEM micrograph of the product powder**

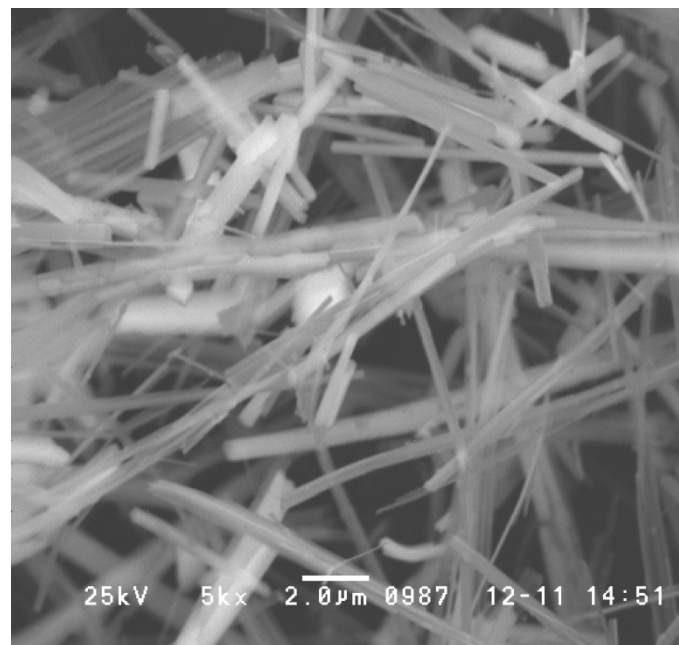
**X-ray diffraction patterns of the product powder**



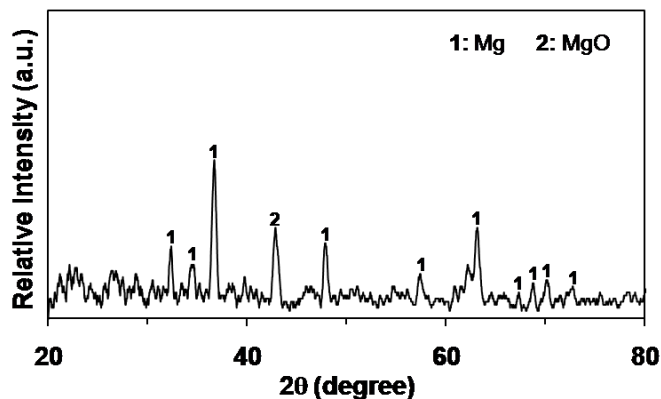
## Synthesis of Mg nanowire by electric furnace



Schematic diagram of the furnace reactor system



SEM micrograph of the product Mg nanowire



X-ray diffraction patterns of the product Mg nanowire

## ***FY 2010 -2011:***

- Search for LiMgN additives to lower H<sub>2</sub> release temperature
- Thermo and kinetic studies of LiMgN with additives cycling using PCT instrument
- Understand the effects of TiH<sub>2</sub> on MgH<sub>2</sub>
- Continue to search new materials based on new concepts.

- Collaborations with the MHCoe Theory Group (U Pitt and Georgia Tech) on reactions mechanisms of hydrogen reactions based on LiMgN,
- Collaboration with SRNL on kinetics of LiMgN
- Collaborations within MHCoe (JPL, Cal Tech) on using NMR for in-depth characterizations,
- Collaborate with Univ of Nevada-Reno on detailed study of phase transformations in Li-Mg-N-H systems.
- Collaborations with SNL on non-equilibrium Mg-Ti-H.
- Collaboration with MHCoe Additive Screening Group on finding additives to improve kinetics.

- Relevance* Discovering and synthesis of solid hydrides that can reversibly store hydrogen.
- Approach* Exploit potentials of ternary nitrides and non-equilibrium alloys of Mg (Mg-Ti)
- Technical Accomplishments and Progress*  
Characterized and studied thermodynamic and kinetic properties of reversible H<sub>2</sub> storage using LiMgN.  
Demonstrated effects of nanosize scale (10 nm) on cyclic H<sub>2</sub> storage of MgH<sub>2</sub> with TiH<sub>2</sub> additive.
- Technology collaborations* Active partnership with theory and analytical characterization group.
- Future plan* Investigate effects of additives on kinetics of H<sub>2</sub> storage using LiMgN.  
Investigate the potential of a new class of materials for H<sub>2</sub> storage (to be disclosed).