Li-Mg-N-H HYDROGEN STORAGE SYSTEMS: — COMPOSITION VARIATION, SORPTION PROPERTIES AND MECHANISTIC STUDY

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Outline

- Characteristic Aspects of the Li-Mg-N-H system;
- Mechanism study on 2LiH-Mg$(NH_2)_2$ via in situ PND;
- Effects of stoichiometry on hydrogen sorption performance;
- Functions of $LiBH_4$ in the enhanced kinetics of 2LiH-Mg$(NH_2)_2$ system
- Conclusions

FuncHy functional materials for mobile hydrogen storage

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Li-Mg-N-H system

- Reversible at 200°C
- ΔH ~40 kJ/mol H_2
- 1 bar-Equilibrium pressure at 90°C

- Slow kinetics
- 1/3 capacity under vacuum

Hydrogen sorption mechanism

In slope region

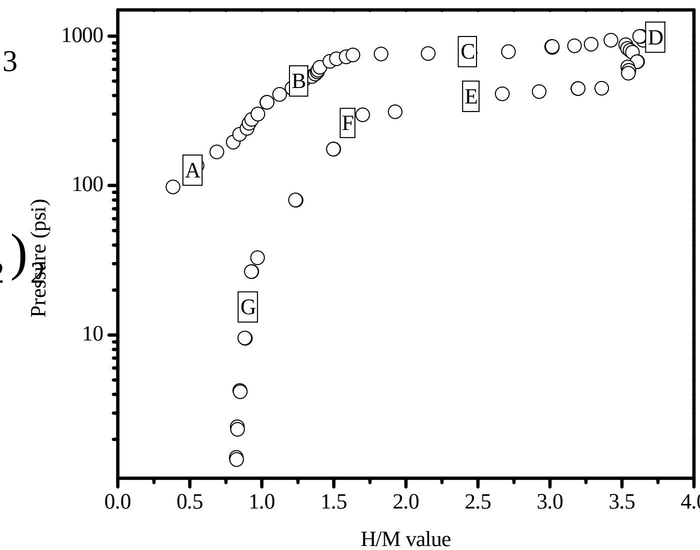
$$2Li_2Mg(NH)_2 + H_2 \leftrightarrow LiH + LiNH_2 + Li_2Mg_2(NH)_3$$

In plateau region

$$LiNH_2 + Li_2Mg_2(NH)_3 + 3H_2 \leftrightarrow 3LiH + 2Mg(NH_2)_2$$

$$Intermediate: Li_2Mg_2(NH)_3$$
$$and\ LiNH_2$$

PCI measurement

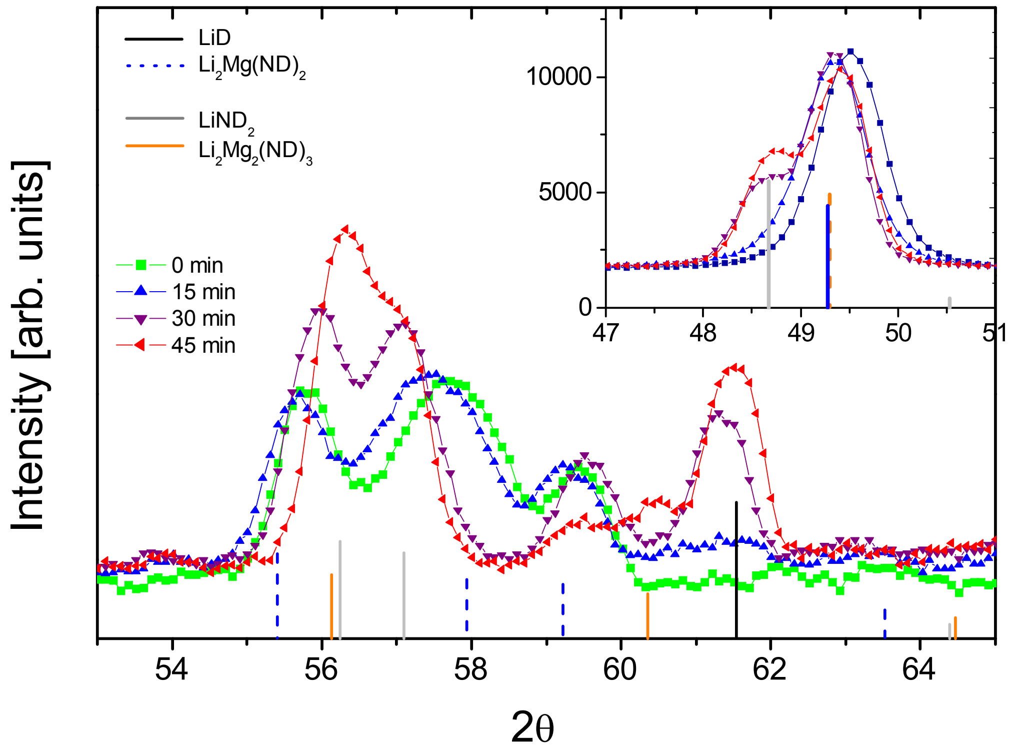


Hu et al, *J. Phys. Chem. C* **2007,** *111,* 18439-18443

Experimental

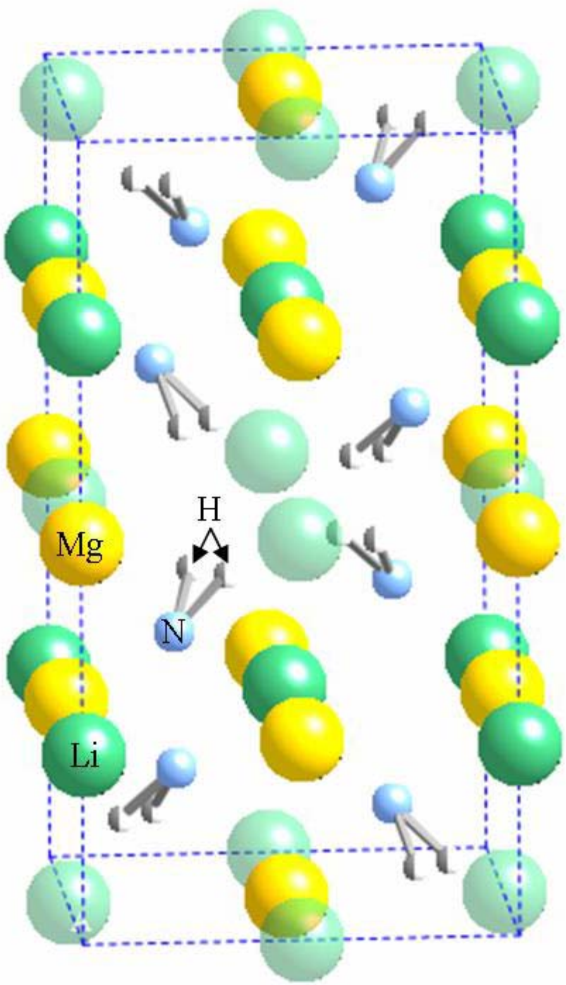
- Synthesis of $Li_2Mg(ND)_2$ by multiple absorption/desorption in D_2 atmosphere;
- Synthesis of $Li_2Mg_2(NH)_3$
- In situ Neutron diffraction measurements of D_2 absorption by $Li_2Mg(ND)_2$ on the D20 at the Institute Laue Langevin reactor source, Grenoble
- Rietvelt refinement for crystal structures

2 - step mechanism



- The amount of Li-Mg-imide (α- and β-modification) decreases quickly after D_2 is added to the sample.
- Li-deuteride is formed at an early stage of the reaction (i.e., prior to the appearance of Mg-amide)
- LiD, $LiND_2$ and $Li_2Mg_2(ND)_3$ were detected upon introduction of D_2

Structure $Li_2Mg_2(NH)_3$

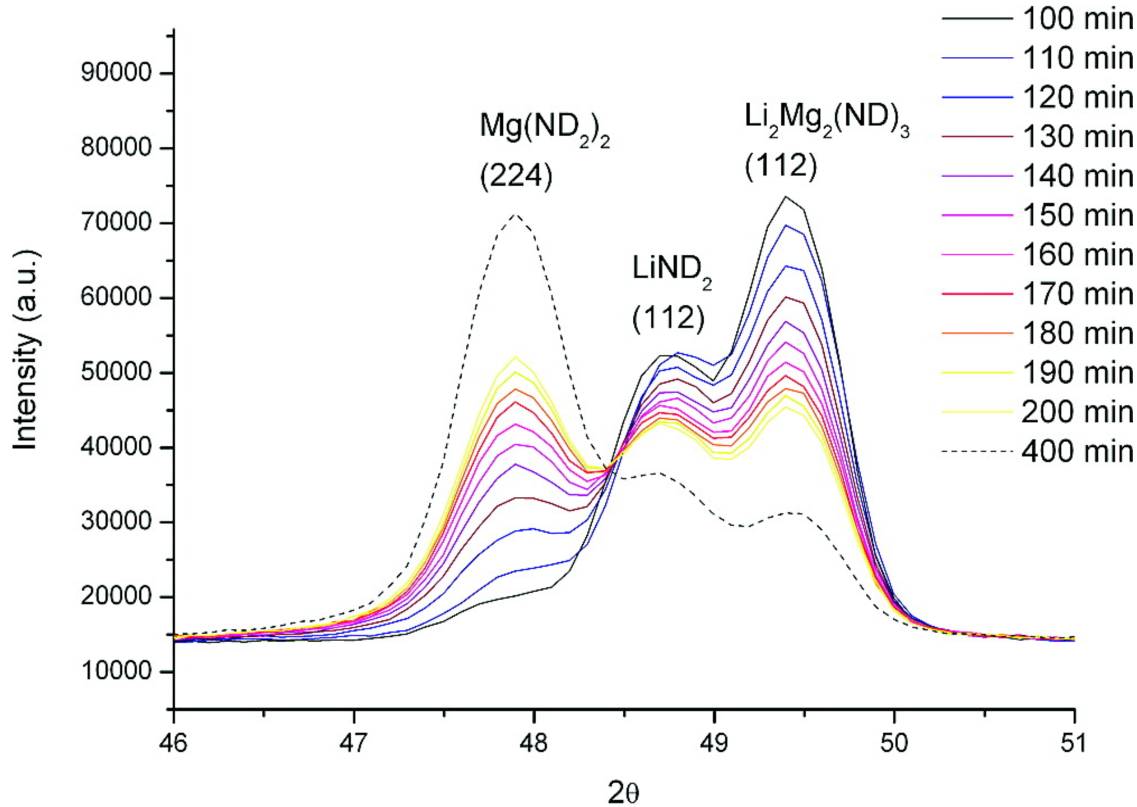


X-ray Diffraction + Neutron Diffraction

space group I-42m (121) a=5.130(3) (Å) , c= 9.619(1)Å

Atom/pos.	*X (Å)*	*Y (Å)*	*Z (Å)*	Occ.
N (8i)	0.270(8)	0.270(8)	0.137(6)	1
D (16j)	0.229(3)	0.141(2)	0.075(1)	0.5
Mg (2b)	0	0	0.5	1
Li (4c)	0	0	0.762(2)	1
Li (4e)	0	0.5	0	0.2
Li/Mg (4d)	0	0.5	0.25	0.2/08

Time-resolved series of diffraction patterns



Time-resolved series of diffraction patterns collected at 70 bar and 225° C. In the angular region shown the intensity change of three reflections due to absorption of deuterium can be observed. Notable is the relatively much stronger decrease in intensity for the reflection of the $Li_2Mg_2(ND)_3$ phase as compared to $LiND_2$.

High Capacity through stoichiometry adjustment?

1:2

$Mg(NH_2)_2 + 2LiH$ —— $Li_2Mg(NH)_2 + 2H_2$ 5.6 wt %

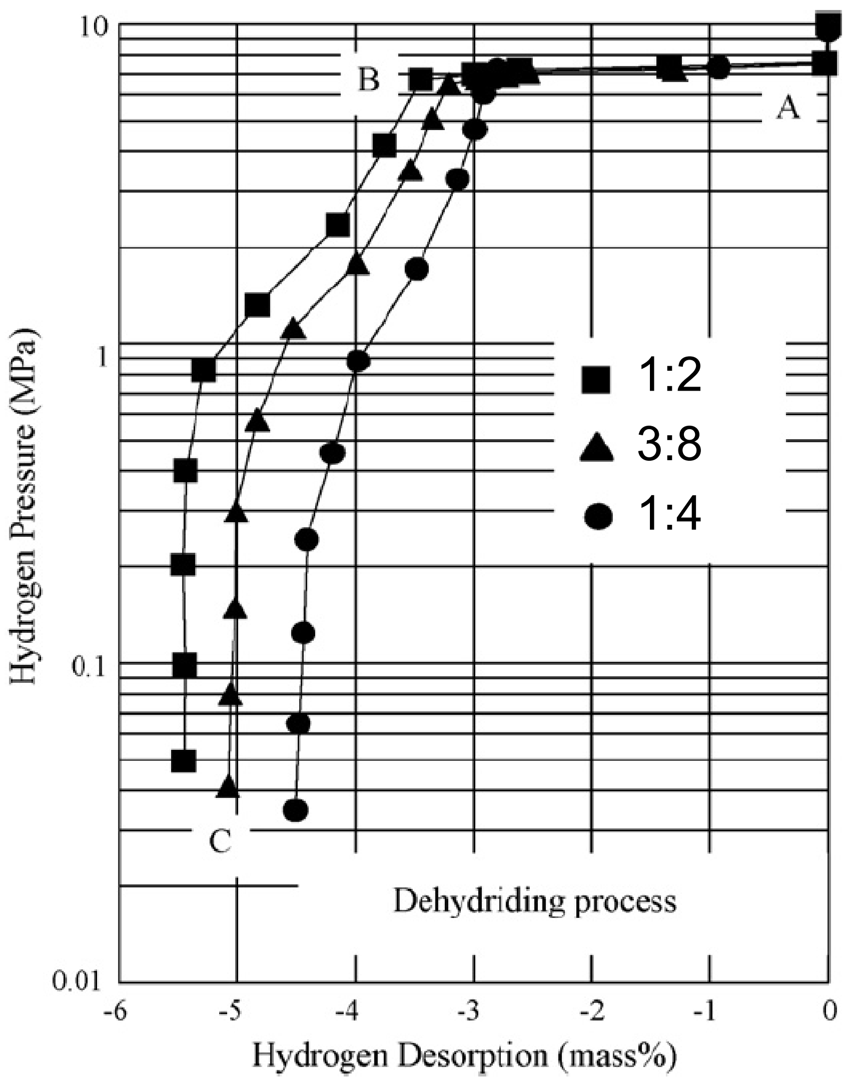
1:2.7 (3:8)

$3\ Mg(NH_2)_2 + 8LiH$ —— $4Li_2NH + Mg_3N_2 + 8H_2$ 6.9 wt %

1:4

$Mg(NH_2)_2 + 4LiH$ —— $4Li_3N + Mg_3N_2 + 12H_2$ 9.1 wt %

Pressure composition isotherms

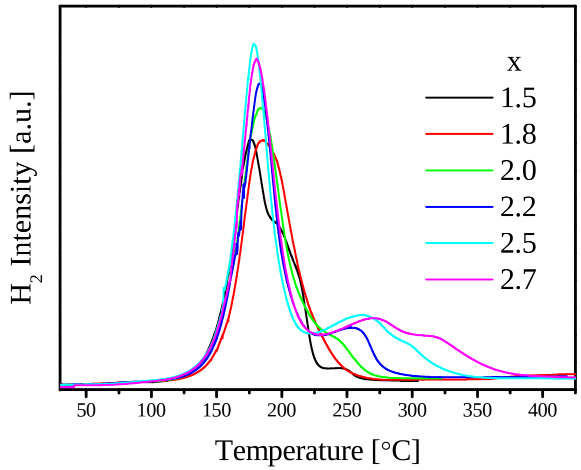


M. Aoki et al., J Alloys Compds 446–447 (2007) 328–331

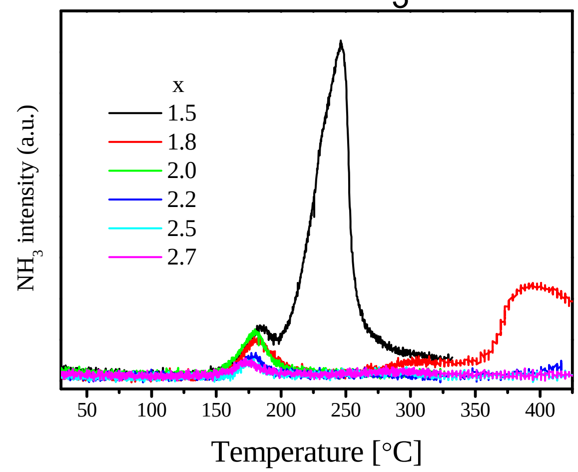
T = 250°C desorption

$Mg(NH_2)_2$ + x LiH x=1.5 – 2.7

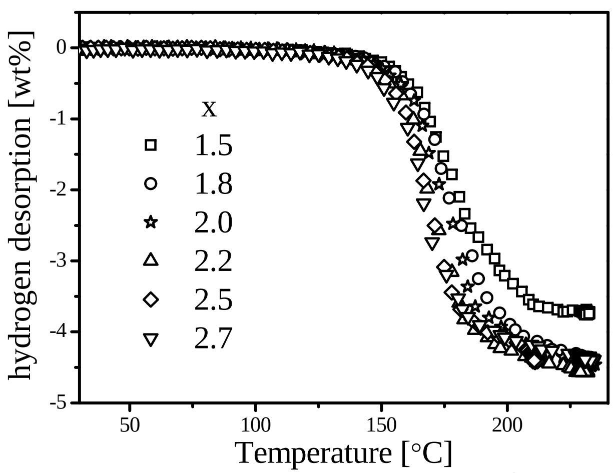
TPD-H_2



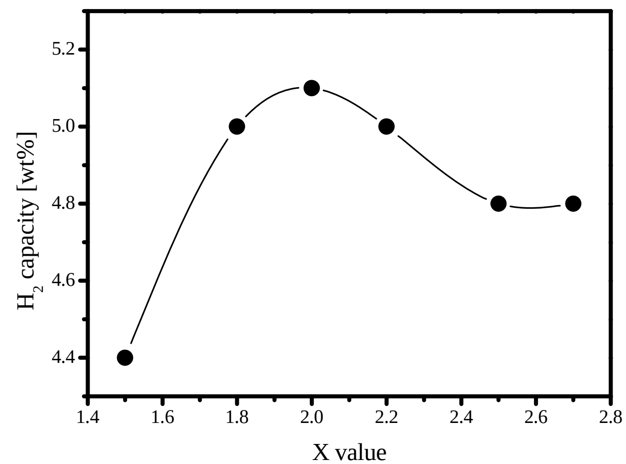
MS-NH_3



Volumetric-H_2

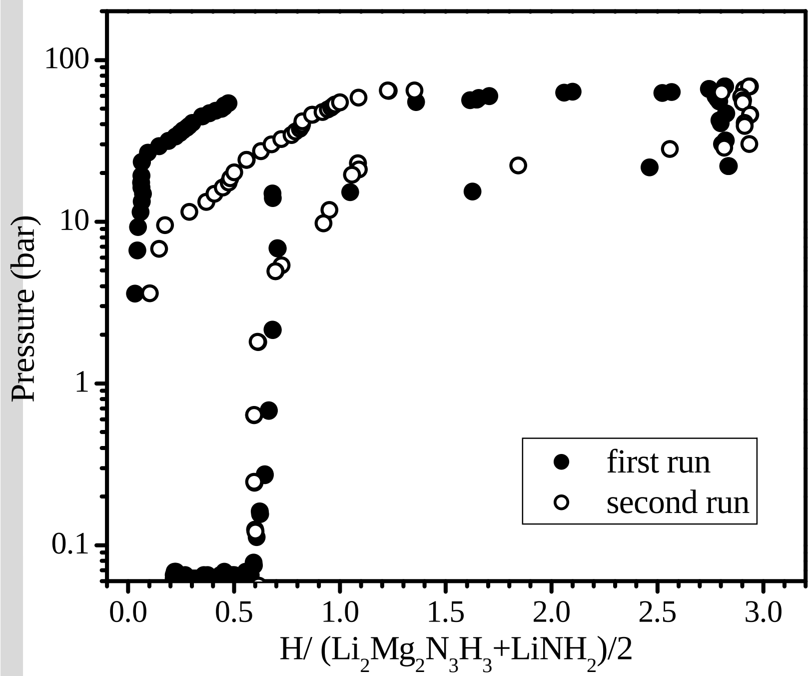


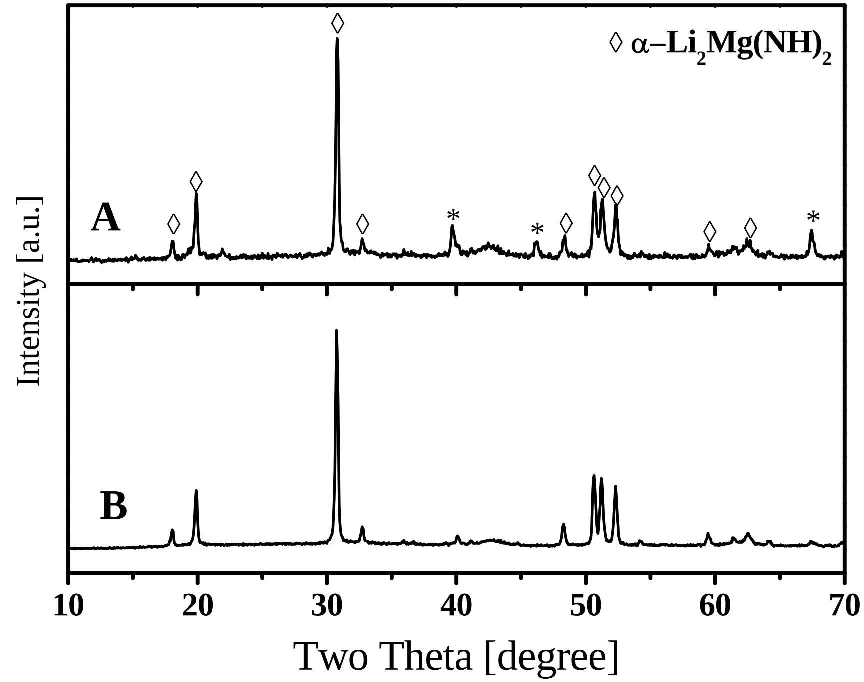
xLiH - H_2



Chem. Mater. 2009, 21, 3485–3490

Cycling $Li_2Mg_2(NH)_3 + LiNH_2$





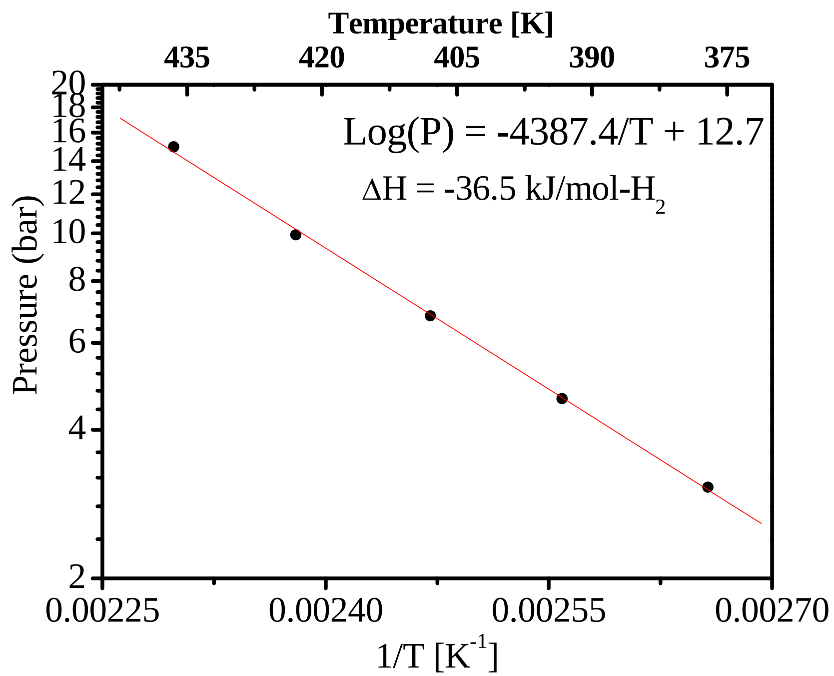
$$Li_2Mg_2(NH)_3 + LiNH_2 \rightarrow 2Mg(NH_2)_2 + 3LiH \qquad X = 1.5$$

⇩

$$Li_2Mg(NH)_2 + NH_3 + H_2$$

Enhanced hydrogen sorption by $LiBH_4$ addition

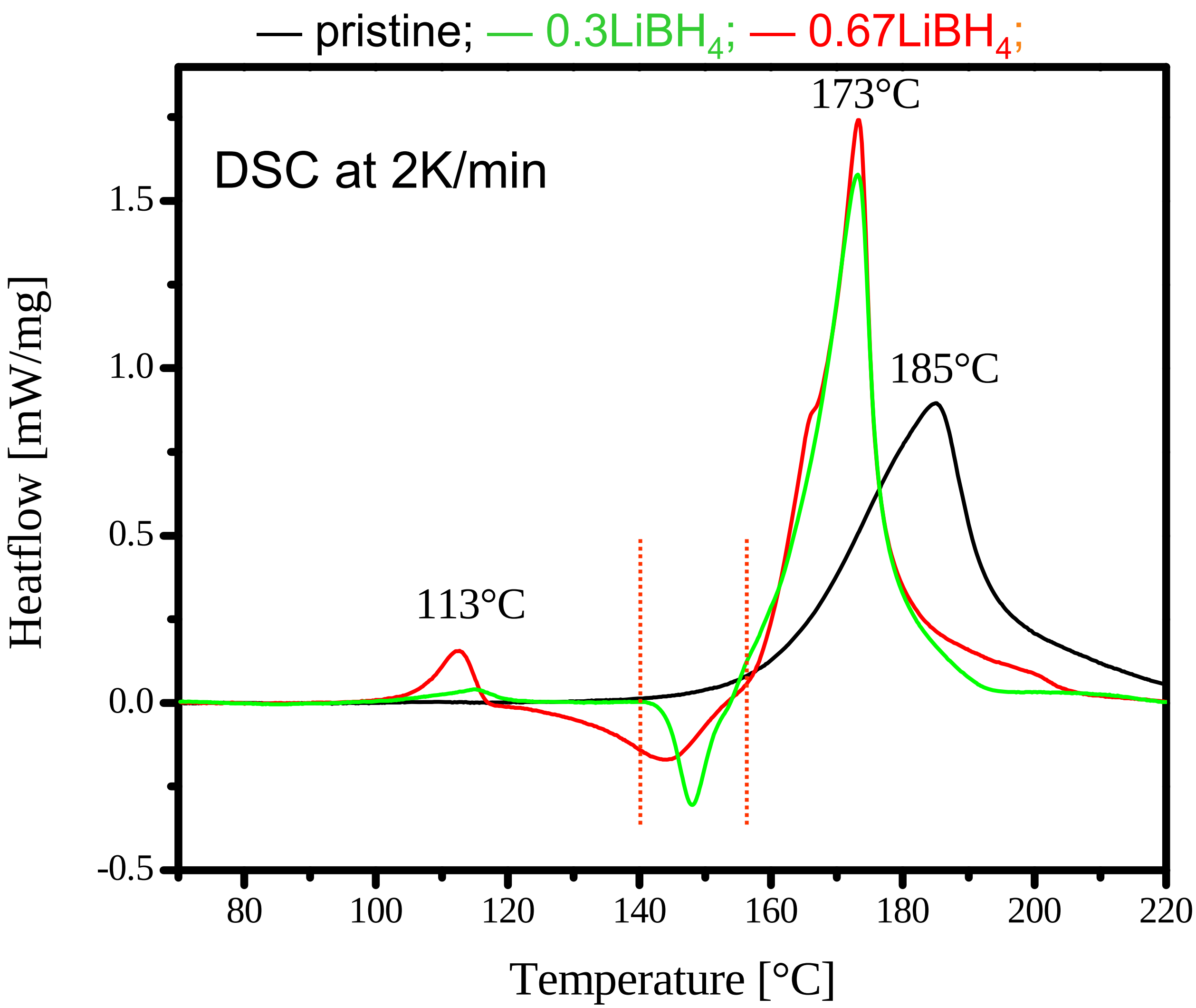
$2LiH\text{-}Mg(NH_2)_2\text{-}0.1LiBH_4$



- **5 wt%, fully reversible**
- **ΔH = 36.5 kJ/mol-H_2**
- **1bar equilibrium H_2 at 70°C (extrapolated)**

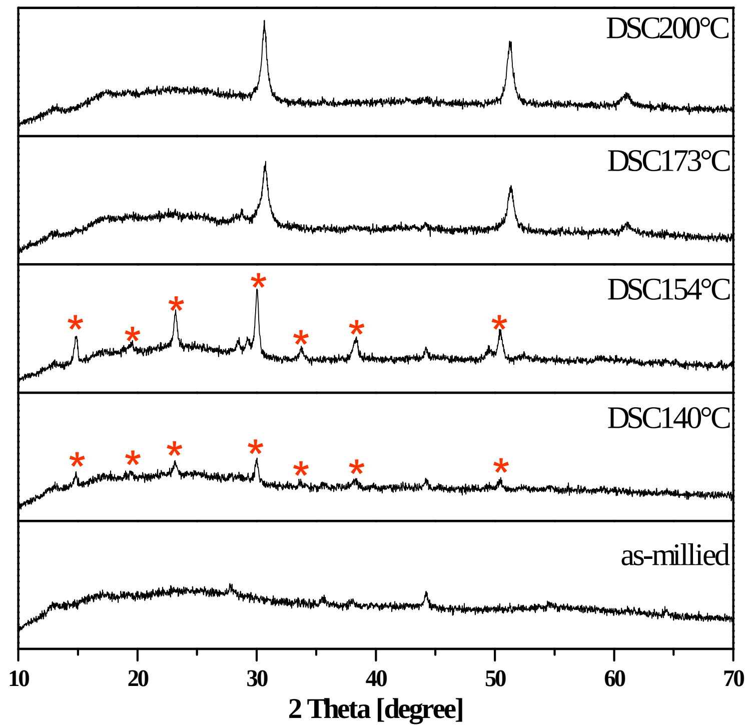
J. J. Hu et al, *Chem. Mater.* **2008,** *20,* 4398–4402

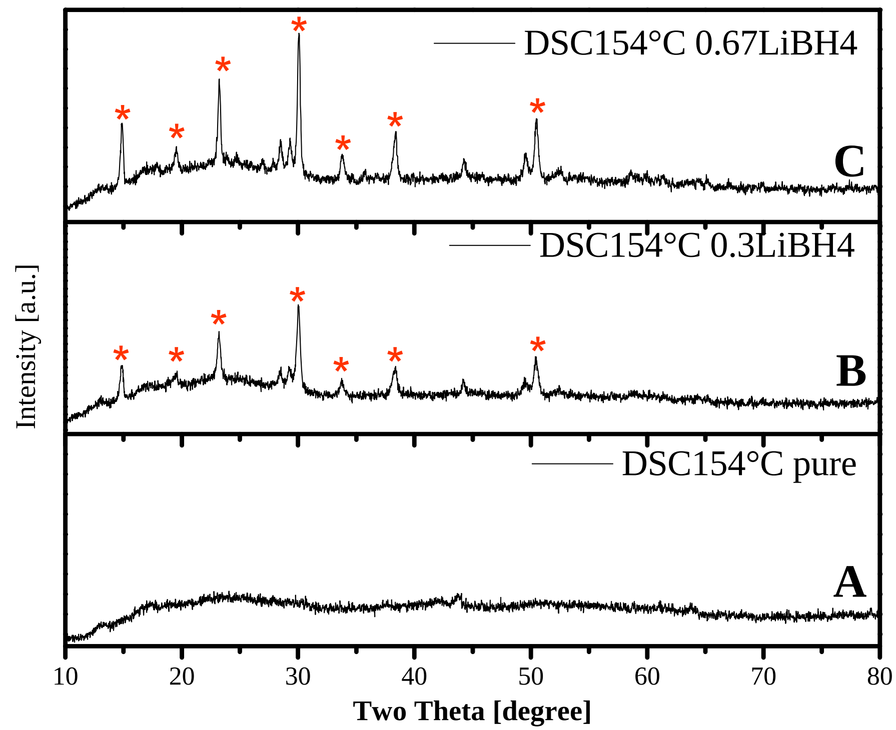
Exothermic event induced by $LiBH_4$ addition



Facilitated Re-crystallization of $Mg(NH_2)_2$

X-ray diffraction patterns





Heteroepitaxy growth of $Mg(NH_2)_2$ on $LiBH_4$ crystal seeds

Intermediate $Li_4(BH_4)(NH_2)_3$ in presence of $LiBH_4$

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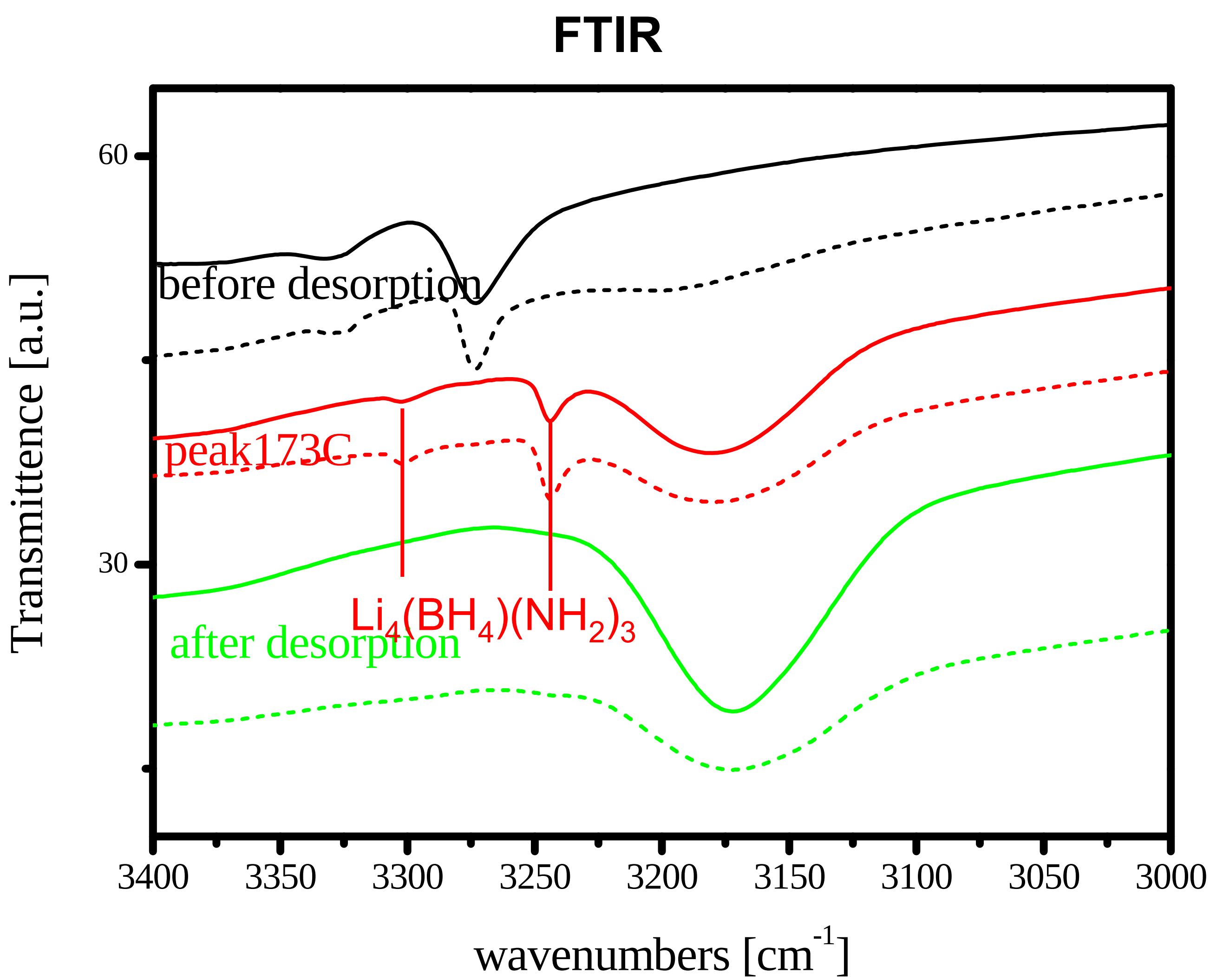
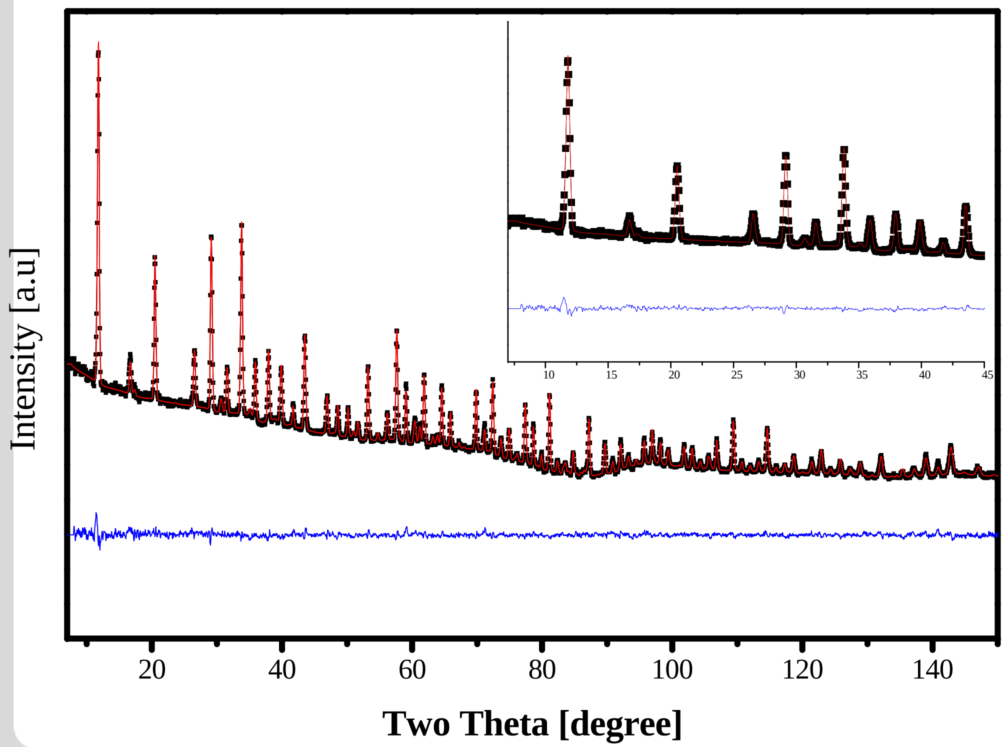


Crystal Structure of $Li_4(^{11}BD_4)(NH_2)_3$ by Powder Neutron Diffraction

- Stoichiometry at 1:3 $Li^{11}BD_4$ / $LiNH_2$
- Annealing above melting temperature 230°C for high crystallinity



Bond angle	
H1-N-H2	105.6(12)
H1-N-H1	106.8(11)
H3-B-H3	108.9(6)
H3-B-H4	110.0(5)

cubic cell : a =10.64678(3)Å.

Conclusions

- In situ observation of 2-step mechanism by PND
- Detection and structure determination of tetragonal intermediate $Li_2Mg_2(NH)_3$ and $Li_4(BH_4)(NH_2)_3$;
- No higher capacity from stoichiometric adjustment without compromise of properties
- Kinetic and thermodynamic improvement by $LiBH_4$ addition

THANK YOU!