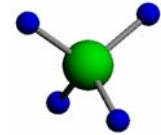


June 19-22, 2005, Lucca, ITALY  
IPHE - Hydrogen Storage Technology Conference

***Advanced Hydrogen Storage Functions of  
Destabilized and Mixed  
Complex Hydrides***



Shin-ichi ORIMO, Yuko NAKAMORI

Institute for Materials Research (IMR)  
Tohoku University

[www.hydrogen.imr.tohoku.ac.jp](http://www.hydrogen.imr.tohoku.ac.jp)

# Research project

*collaborated with*



**TOYOTA CRDL, INC.**

S. Towata

[www.tytlabs.co.jp](http://www.tytlabs.co.jp)

*supported by*



*“Development for Safe Utilization  
and Infrastructure of Hydrogen”*

[www.nedo.go.jp/index.html](http://www.nedo.go.jp/index.html)

*communicated with*

E. Akiba, AIST-Tsukuba  
H. Fujii, Hiroshima Univ.  
C.M. Jensen, Univ. Hawaii  
T. Kiyobayashi, AIST-Kansai  
D.K. Ross, Univ. Salford  
G. Sandrock, Sunatech.  
S. Suda, Kogakuin/MERIT  
H.T. Takeshita, Kansai Univ.  
J.C.F. Wang, K.J. Gross, SNL  
R. Zidan, SRNL  
A. Züttel, Univ. Fribourg

*focused on*

1. Destabilization of  $\text{LiBH}_4$  and  $\text{LiNH}_2$
2. Combination of amide and hydride
3. Prevention of  $\text{NH}_3$ -contamination
4. Provision of new reaction pathway

# Trinary collaboration



Ultrasoft-pseudopotential based on DFT (GGA)

## Theory

K. Miwa, N. Ohba  
First-Principles Calculation and Simulation

## Material Synthesis

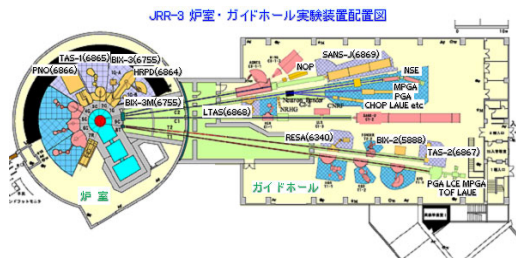
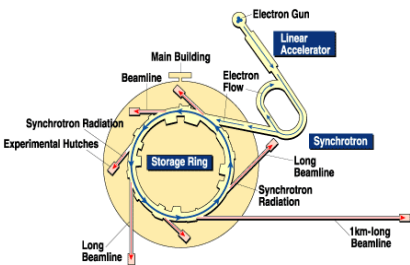
Y. Nakamori, M. Aoki  
Solid-gas reaction, Milling Evaporation



## Analysis

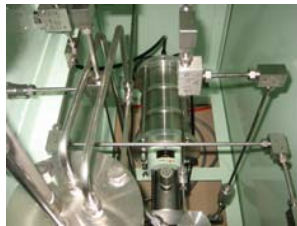
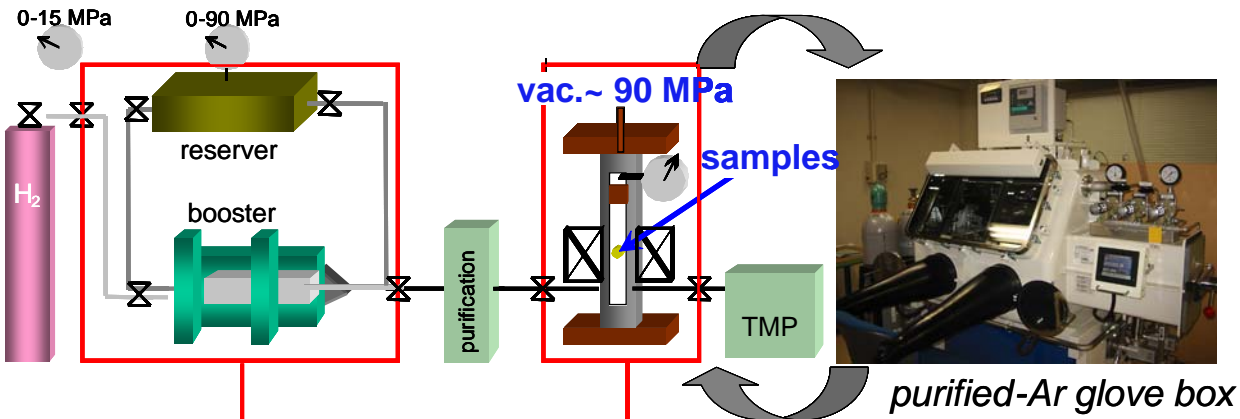
T. Noritake, G. Kitahara, A. Ninomiya, K. Ohyama

SR and Neutron Diffractions *In-situ* Characterization



# Metallurgical material synthesis

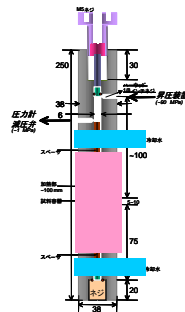
## 1) reactive synthesis (or sintering)



hydrogen booster  
(without electricity)



reaction cell



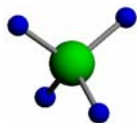
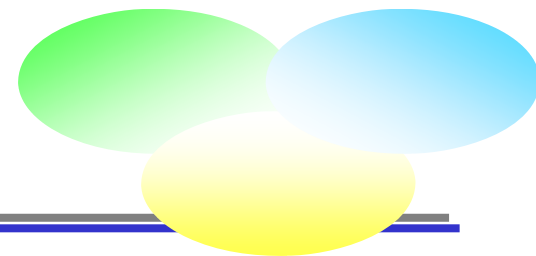
## 2) evaporation



## 3) milling



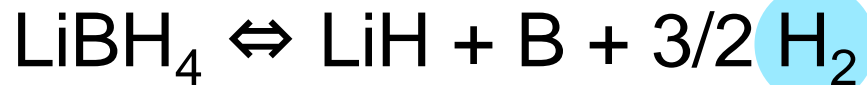
# 4 Guidelines



1. Destabilization of  $\text{LiBH}_4$  and  $\text{LiNH}_2$   
*cation with larger electronegativity*
2. Combination of amide and hydride  
*lower  $T_d$  / faster reaction with “ $\text{NH}_3$ ”*
3. Prevention of  $\text{NH}_3$ -contamination  
*“tunable” composition / starting material*
4. Provision of new reaction pathway  
*intermediate phase formed by dehydrating*

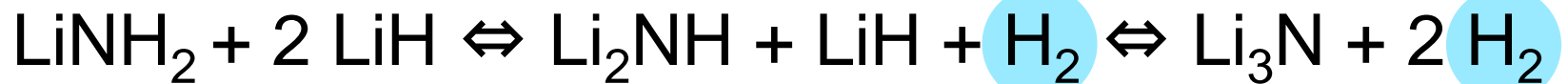
# Dehydrating reaction

A. Züttel, S. Rentsch, P. Fischer, P. Wenger, P. Sudan, Ph. Mauron and Ch. Emmenegger,  
*J. Alloys Compd.* 356-357 (2003) 515



69 (74 \*)  
kJ/molH<sub>2</sub>      \*obtained from  
                                 calculation

P. Chen Z. Xiong, J. Luo, J. Lin, K.L. Tan, *Nature* 420 (2002) 302



45~60 (78\*)  
kJ/molH<sub>2</sub>

116 (124\*)  
kJ/molH<sub>2</sub>

~ 10 mass% H<sub>2</sub>

dehydrating temp. > 473-550 K

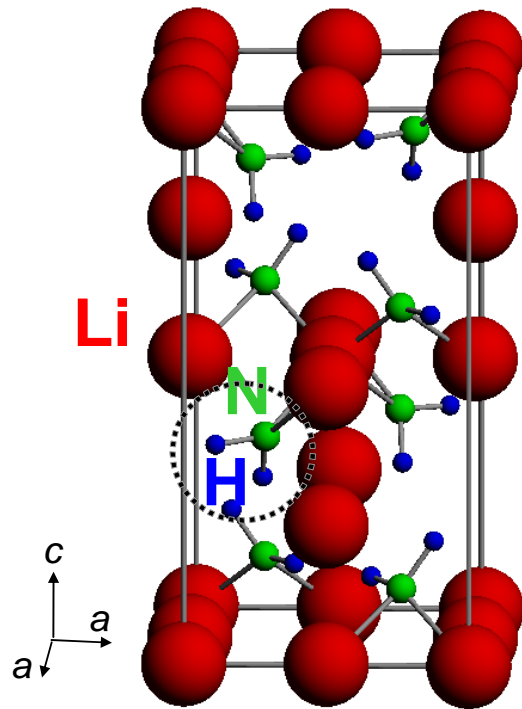
IEA target temp. < 353 K

# Atomic and electronic structures



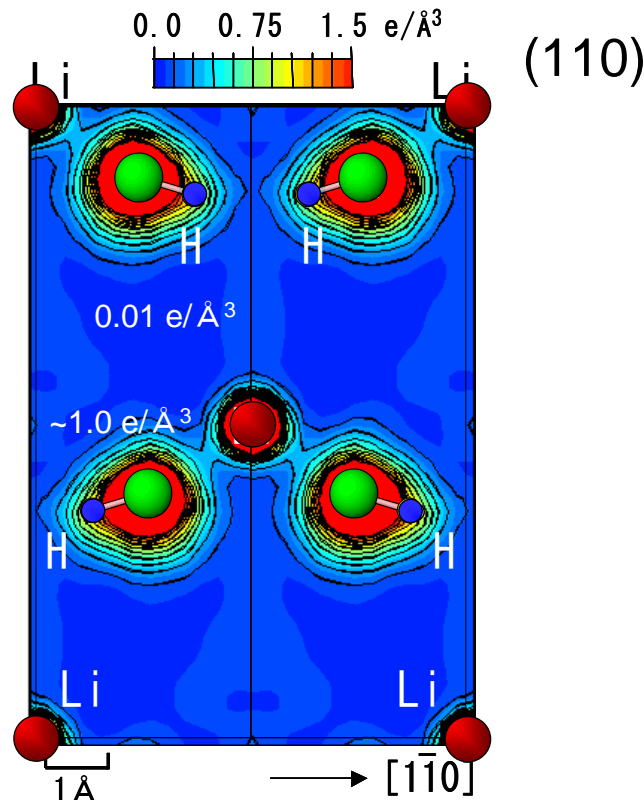
Tetra.,  $I\bar{4}$  (No. 82)

$a = 0.5037$  nm  
 $c = 1.0278$  nm



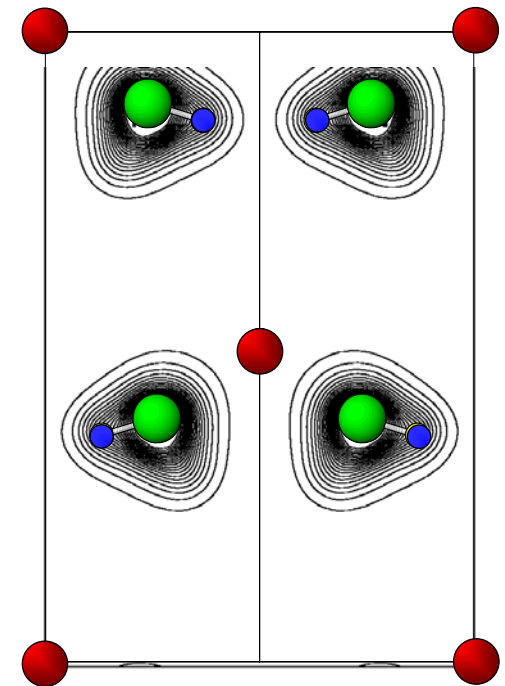
V.H. Jacobs, R. Juza,  
*Z. Anorg. Allg. Chem.*  
391 (1972) 271

SR-XRD & MEM  
(Spring-8, JAPAN)



T. Noritake, H. Nozaki, M. Aoki, S. Towata,  
G. Kitahara, Y. Nakamori, S. Orimo,  
*J. Alloys Compd.* 393 (2005) 264.

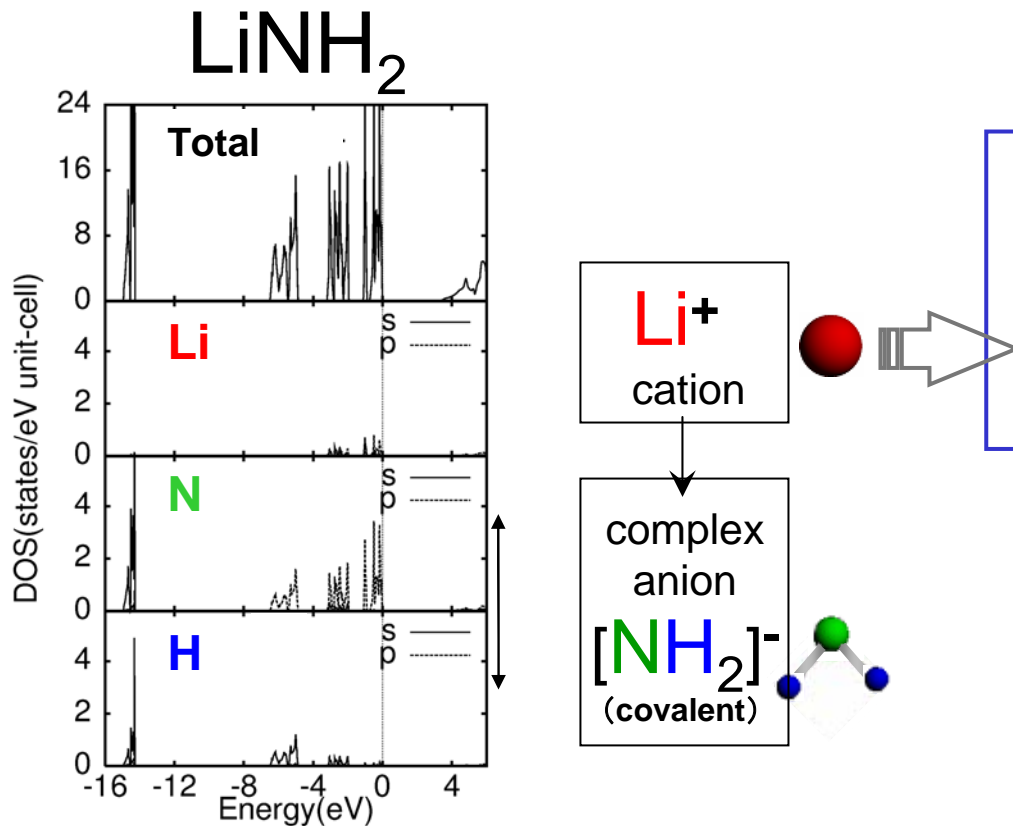
First-Principles  
Calculation



K. Miwa, N. Ohba, S. Towata,  
Y. Nakamori, S. Orimo,  
*Phys. Rev. B* 71 (2005) 195109



# Charge transfer



cation substitution...

cation <i>M</i>	valence	ionic radius	electro- negativity
Li	1+	0.068 nm	1.0
Mg	2+	0.066 nm	1.2

by the other element with  
**larger  
electronegativity**

Proposed in E-MRS 2003,  
Strasbourg, June 10-13, 2003

S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba,  
T. Noritake, S. Towata, *Appl. Phys. A (Rapid Commun.)*  
79 (2004) 1765

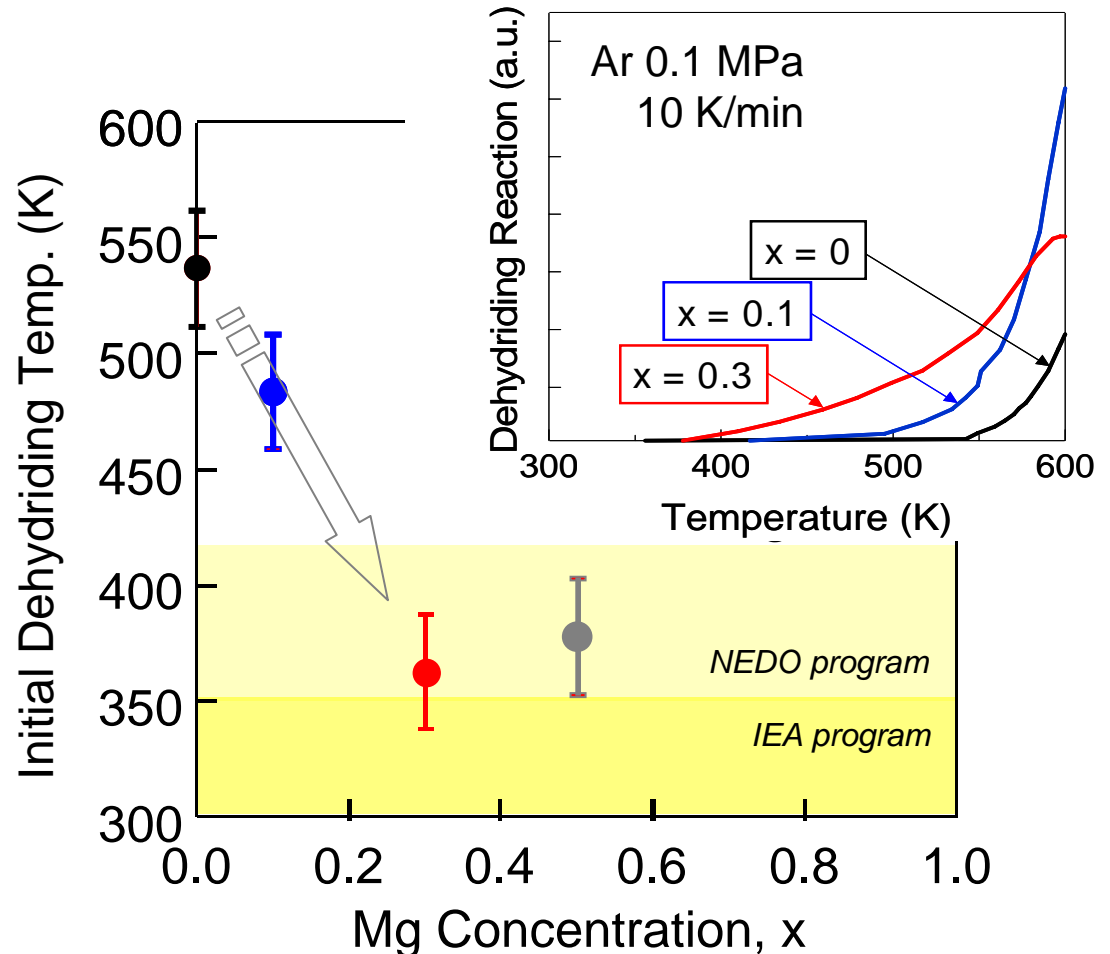
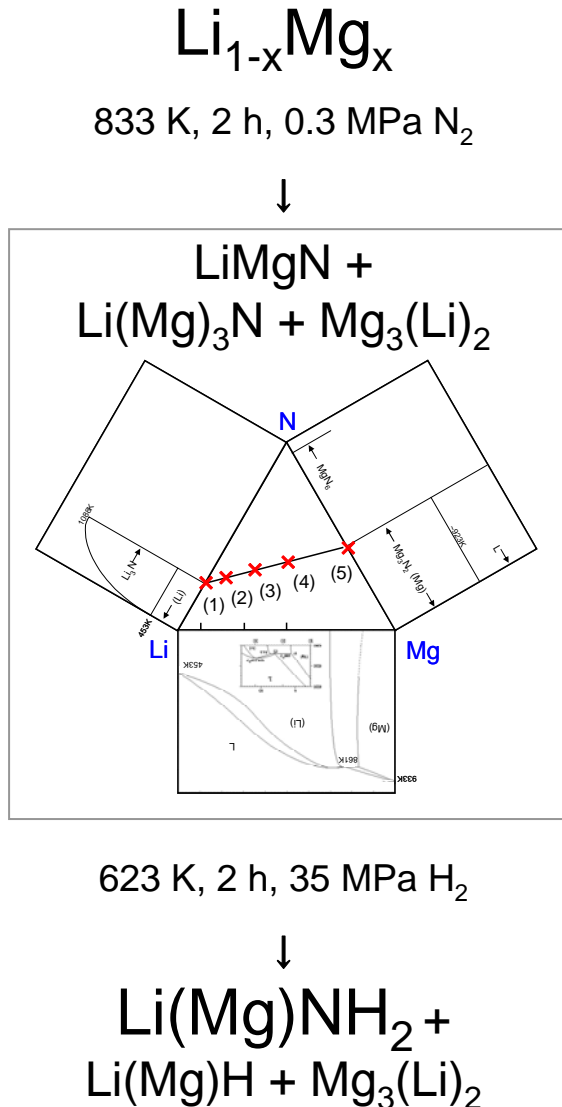
K. Miwa, N. Ohba, S. Towata, Y. Nakamori, S. Orimo,  
*Phys. Rev. B* 71 (2005) 195109

Y. Nakamori, S. Orimo,  
*Mater. Eng. Sci. B* 108 (2004) 51

Y. Nakamori, S. Orimo,  
*J. Alloys Comp.* 370 (2004) 271



# Dehydrating temperatures

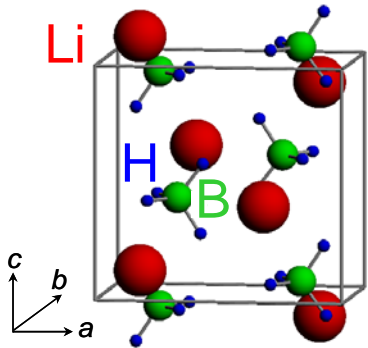


S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, T. Noritake, S. Towata, *Appl. Phys. A (Rapid Commun.)* 79 (2004) 1765-1767

# Mg substitution in LiBH<sub>4</sub>

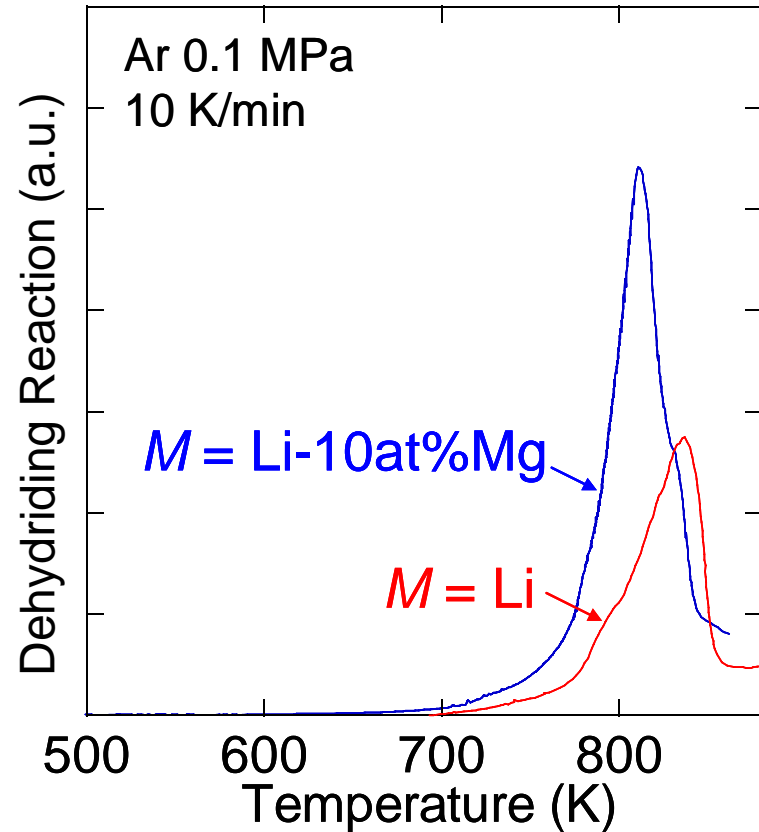
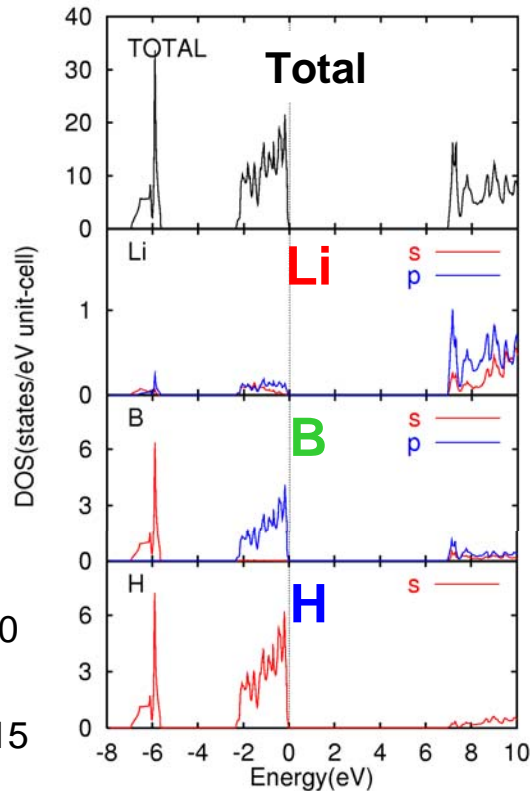


Ortho., *Pnma* (No. 62)  
 $a = 0.718$  nm  
 $b = 0.444$  nm  
 $c = 0.680$  nm, at 408 K



J-Ph. Soulié et al.,  
*J. Alloys Compd.* 346 (2002) 200

A. Züttel et al.,  
*J. Alloys Compd.* 356 (2003) 515



A. Züttel et al.,  
*J. Alloys Compd.*  
(to be submitted)

K. Miwa, N. Ohba, S. Towata,  
Y. Nakamori, S. Orimo,  
*Phys. Rev. B* 69 (2004) 245120

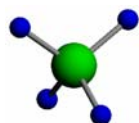
S. Orimo, Y. Nakamori, G. Kitahara,  
K. Miwa, N. Ohba, S. Towata, A. Züttel,  
*J. Alloys Compd.*, in press

# 4 Guidelines

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1. Destabilization of  $\text{LiBH}_4$  and  $\text{LiNH}_2$



2. Combination of amide and hydride  
*lower  $T_d$  / faster reaction with “ $\text{NH}_3$ ”*

3. Prevention of  $\text{NH}_3$ -contamination

4. Provision of new reaction pathway

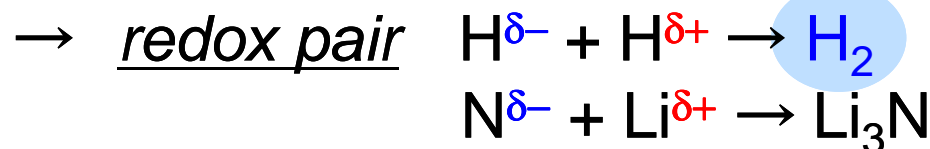
# Amide and hydride

..... dehydrating process .....>			Ideal Hydrogen (mass%)	Ref.
Hydriding	Partial Dehyd.	Dehyd.		
$\text{LiNH}_2 + 2\text{LiH}$	$\text{Li}_2\text{NH} + \text{LiH} + \text{H}_2$	$\text{Li}_3\text{N} + 2\text{H}_2$	10.4	Dafert et al., <i>Monatsh. Chem.</i> (1910), Chen et al., <i>Nature</i> (2002)
$\text{Ca}_2\text{NH} + \text{CaH}_2$	$\text{CaNH} + 2\text{H}_2$		2.1	
$\text{LiNH}_2 + \text{NaH}$	$\text{LiNaNH} + \text{H}_2$		4.2	Ichikawa et al., <i>JPCChem B</i> (2004)
$2\text{LiNH}_2 + \text{MgH}_2$	$\text{Li}_2\text{Mg}(\text{NH})_2 + 2\text{H}_2$		5.6	Luo, <i>JALCOM</i> (2004) Wang, <i>DOE Report</i> (2004)
$3\text{Mg}(\text{NH}_2)_2 + 12\text{LiH}$	$\text{Mg}_3\text{N}_2 + 4\text{Li}_2\text{NH} + 4\text{LiH} + 8\text{H}_2$	$\text{Mg}_3\text{N}_2 + 4\text{Li}_3\text{N} + 12\text{H}_2$	9.1	Nakamori et al., <i>Appl. Phys. A, J. Power Sources</i> (2004)
$3\text{Mg}(\text{NH}_2)_2 + 8\text{LiH}$	$\text{Mg}_3\text{N}_2 + 4\text{Li}_2\text{NH} + 8\text{H}_2$		7.0	Leng et al., <i>JPCChem B</i> (2004)
$3\text{Mg}(\text{NH}_2)_2 + 6\text{LiH}$	$3\text{Li}_2\text{Mg}(\text{NH})_2 + 6\text{H}_2$		5.6	Luo et al., <i>MH2004</i> , Xiong et al., <i>Adv. Mater.</i> (2004)

and so on...

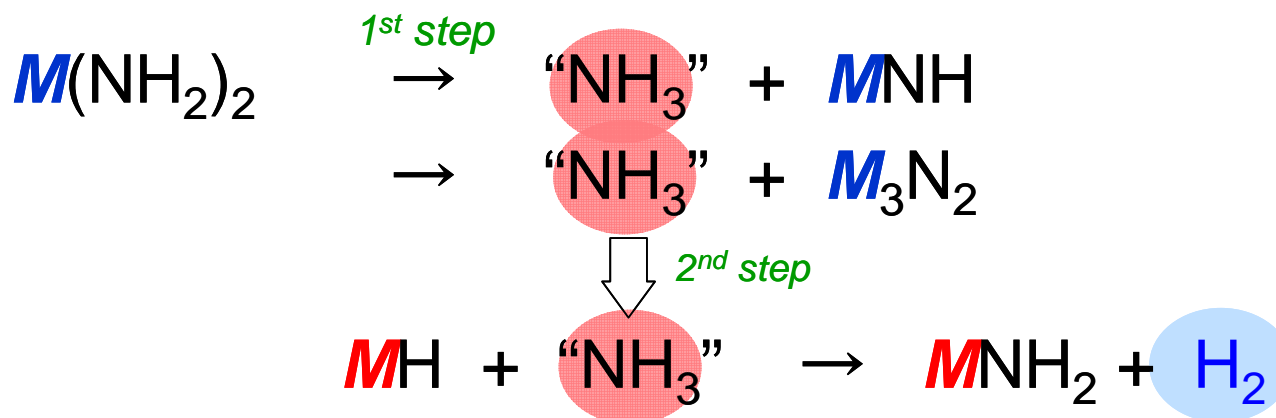
# Dehydrating process

“redox process”



P. Chen, Z. Xiong, J. Luo, J. Lin, K.L. Tan, *J. Phys. Chem. B* 107 (2003) 10967

“NH<sub>3</sub> mediating process”

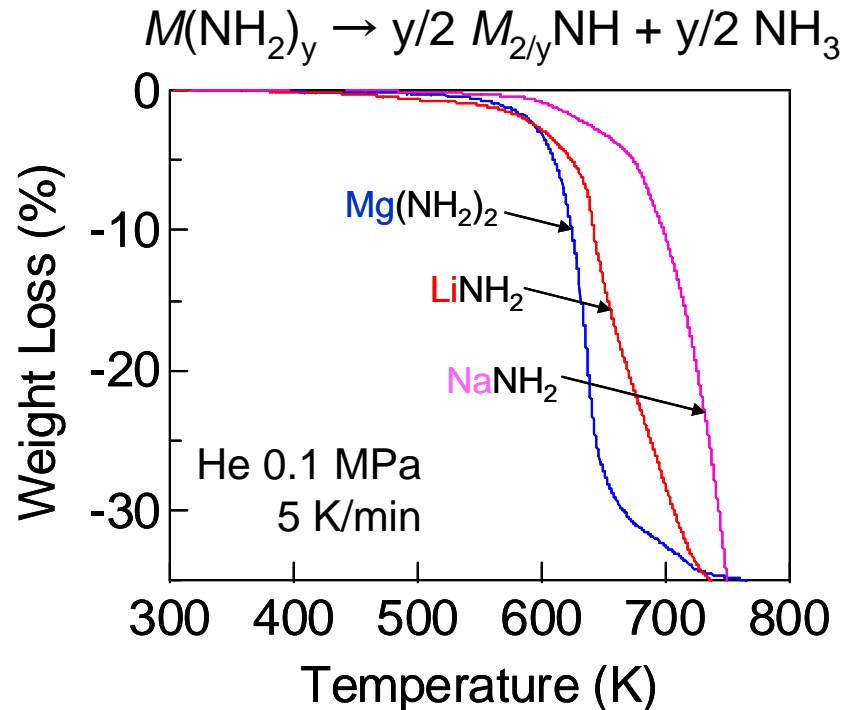


Y.H. Hu, E. Ruckenstein, *J. Phys. Chem. A* 107 (2003) 9737

T. Ichikawa, N. Hanada, S. Isobe, H. Leng, H. Fujii, *J. Phys. Chem. B* 108 (2004) 7887

# 1<sup>st</sup> step (formation of “NH<sub>3</sub>”)

Point : **M**NH<sub>2</sub> with lower decomp. temp.  $T_d$

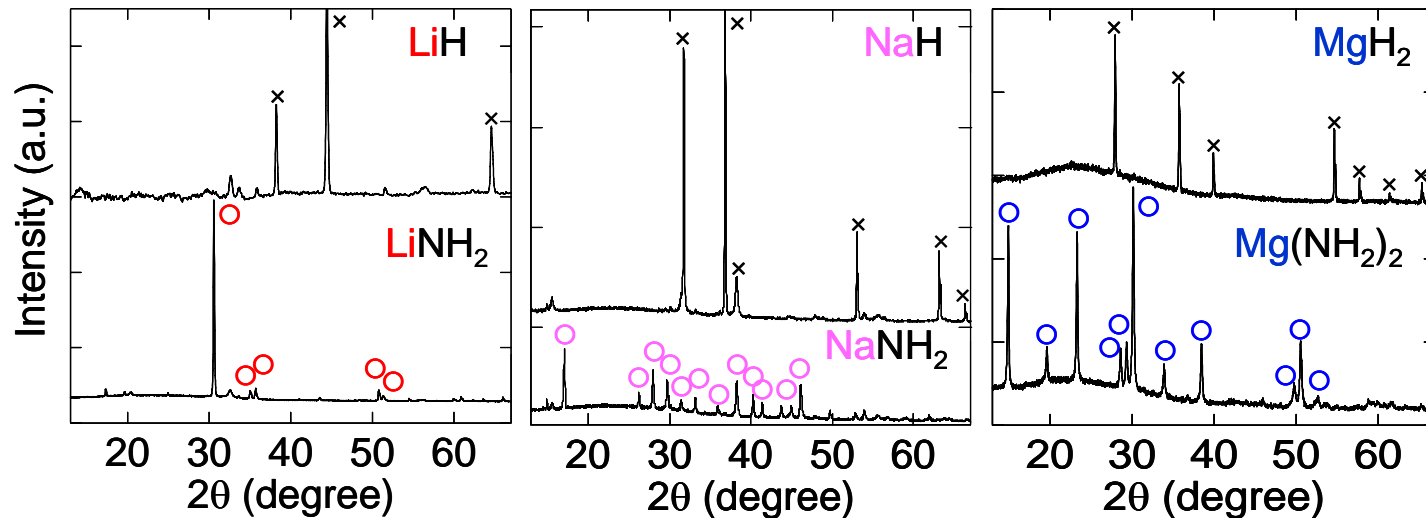
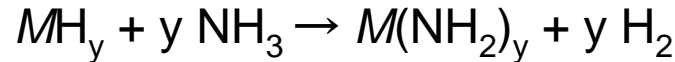


$T_d$  : **Mg**(NH<sub>2</sub>)<sub>2</sub> < **Li**NH<sub>2</sub> < **Na**NH<sub>2</sub>

→ **Mg** for **M**

# 2<sup>nd</sup> step (H<sub>2</sub> emission)

**Point:** **M**H with faster reaction with “NH<sub>3</sub>”



<i>M</i> H	temp. (K)	time (hour)
LiH	493	12
NaH	573	48
MgH <sub>2</sub>	613	168

→ **Li** for **M**

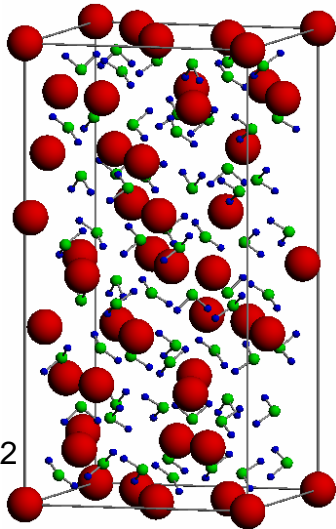
Y. Nakamori et al.,  
*Mater. Trans.*, in press



# Optimized combination

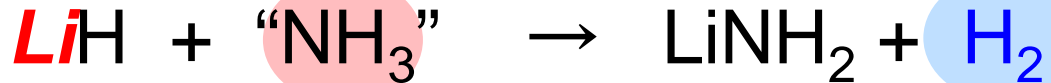


Lower  
decomposition  
temp.

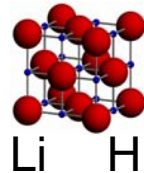


NH<sub>2</sub>

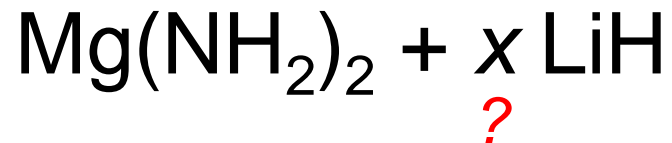
Mg



faster  
reaction  
with “NH<sub>3</sub>”



Li H



?

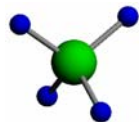
*composition ratio*

# 4 Guidelines



1. Destabilization of  $\text{LiBH}_4$  and  $\text{LiNH}_2$

2. Combination of amide and hydride

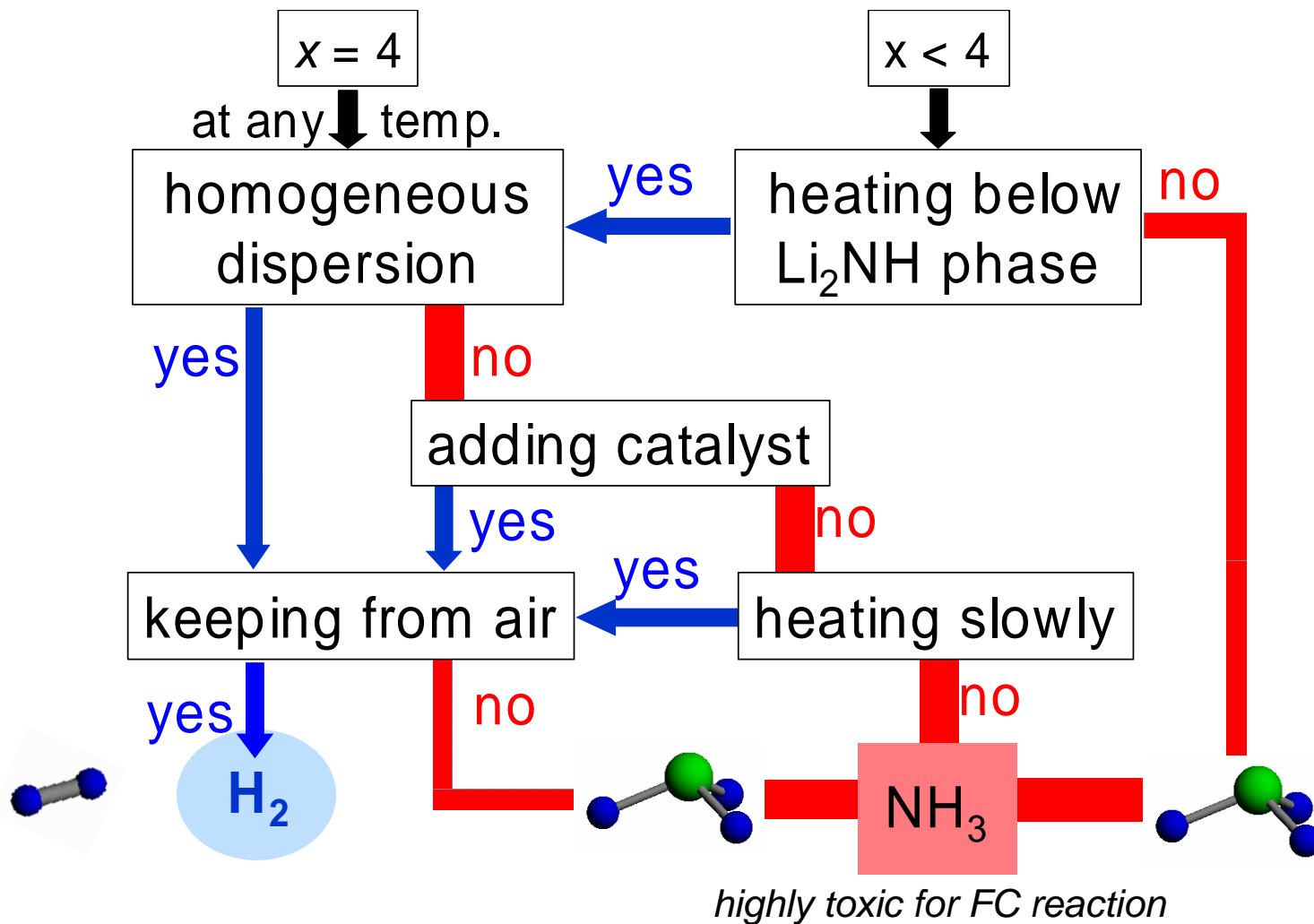


3. Prevention of  $\text{NH}_3$ -contamination

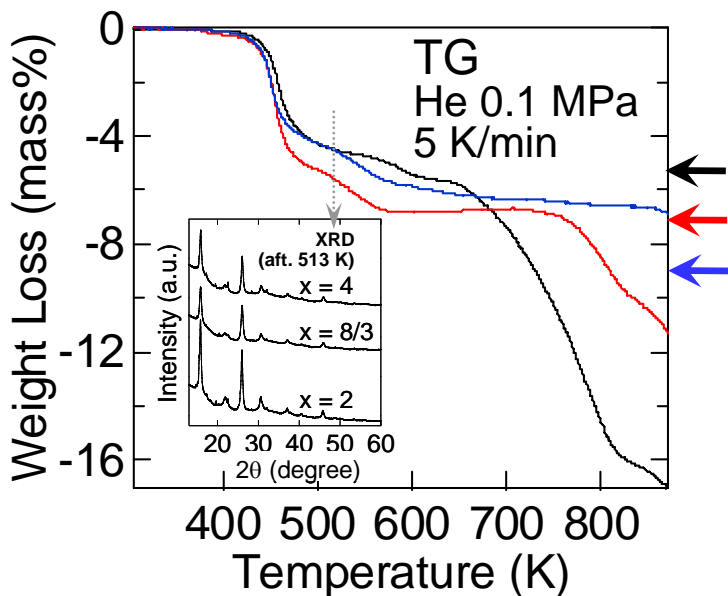
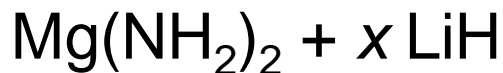
*“tunable” composition / starting material*

4. Provision of new reaction pathway

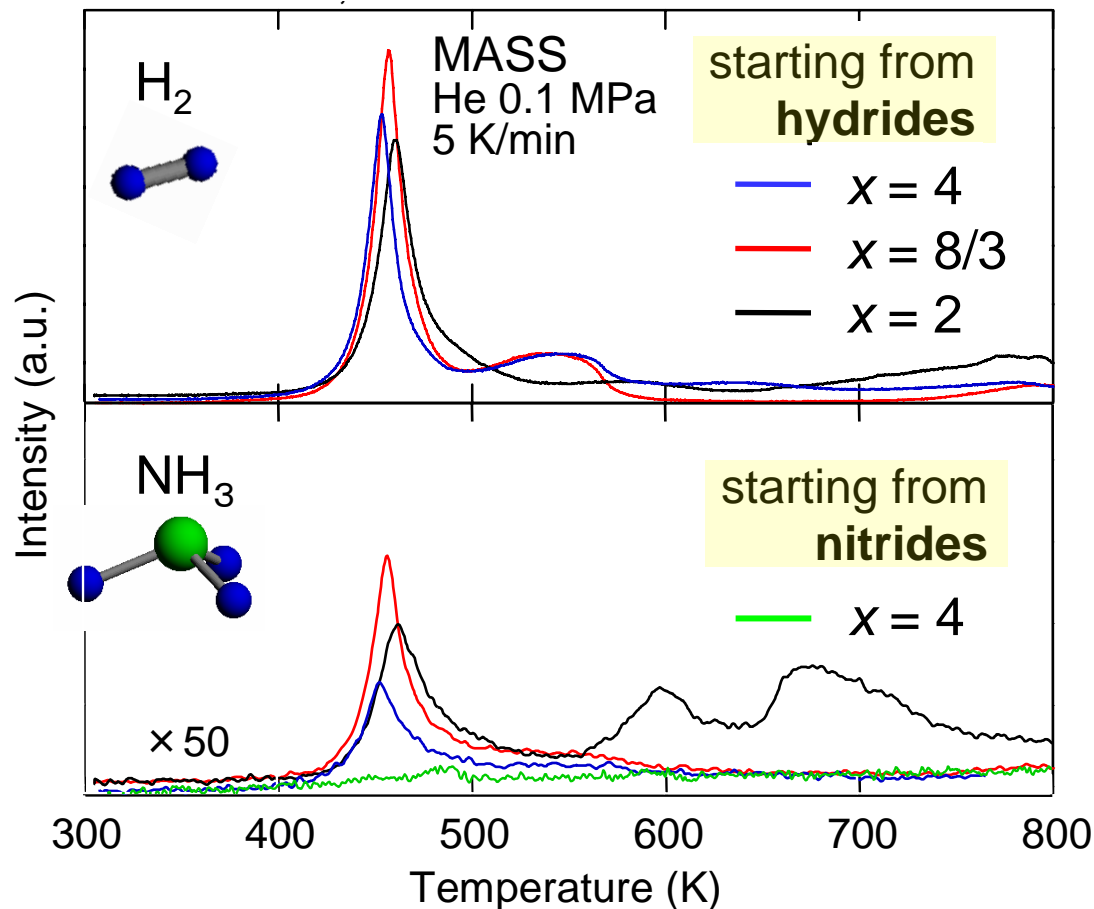
# H<sub>2</sub> / NH<sub>3</sub> from Mg(NH<sub>2</sub>)<sub>2</sub> + x LiH



# Affected by composition *and* ...

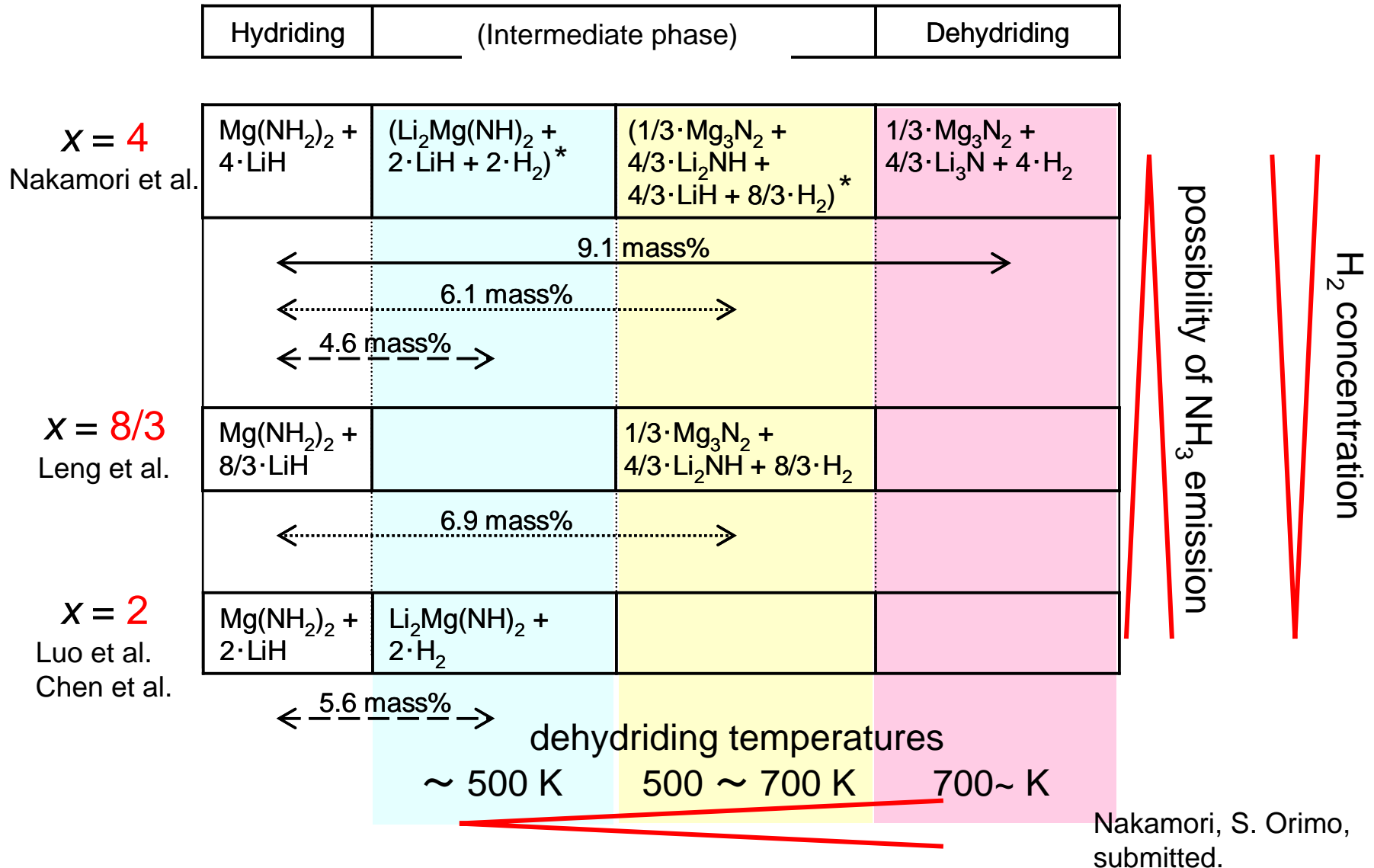


- x = 4 (max. 9.1 mass%)
- x = 8/3 (max. 6.9 mass%)
- x = 2 (max. 5.6 mass%)





# x, depending on applications



# 4 Guidelines



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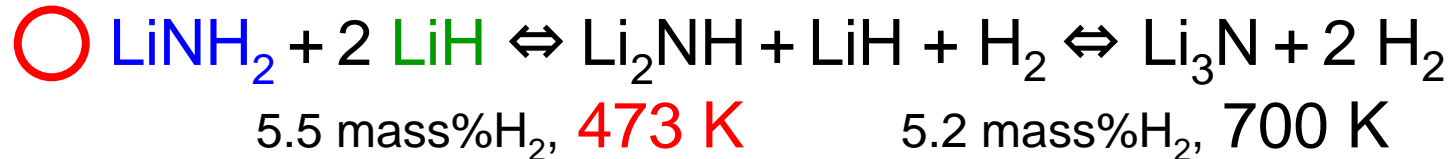
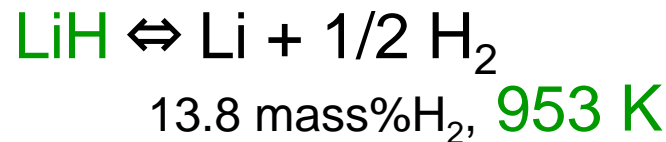
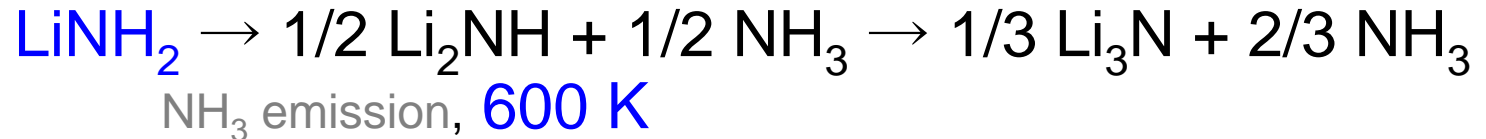
4. Provision of new reaction pathway

*Intermediate phase formed by dehydriding*



# Mixing effect

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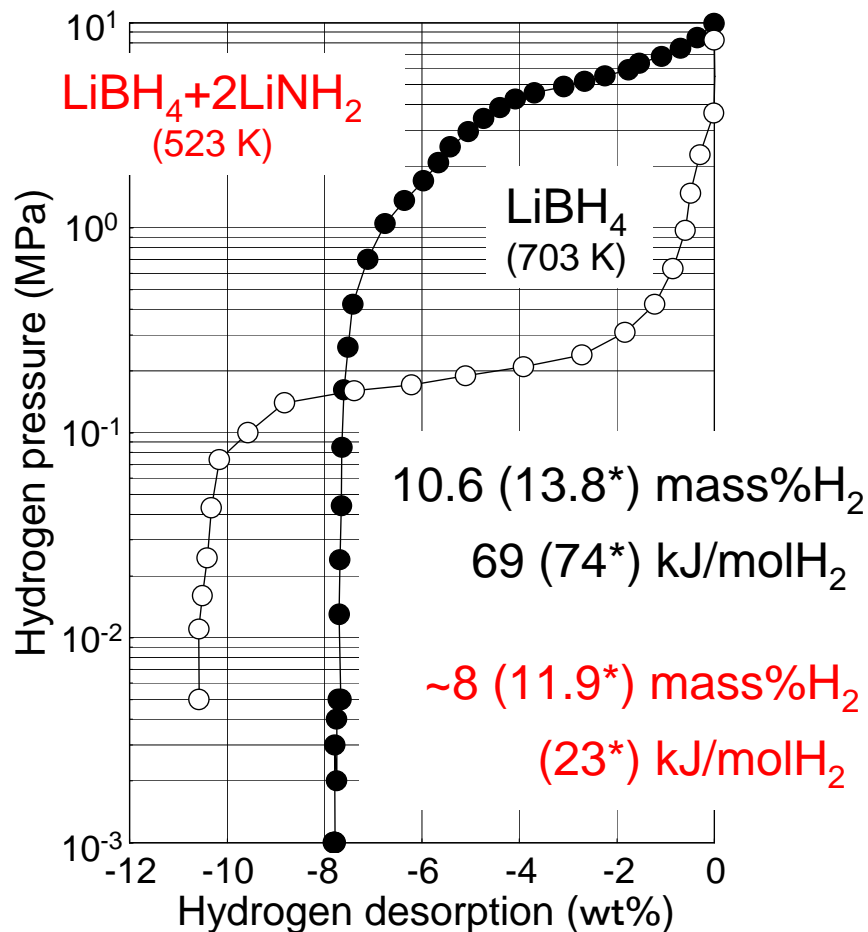
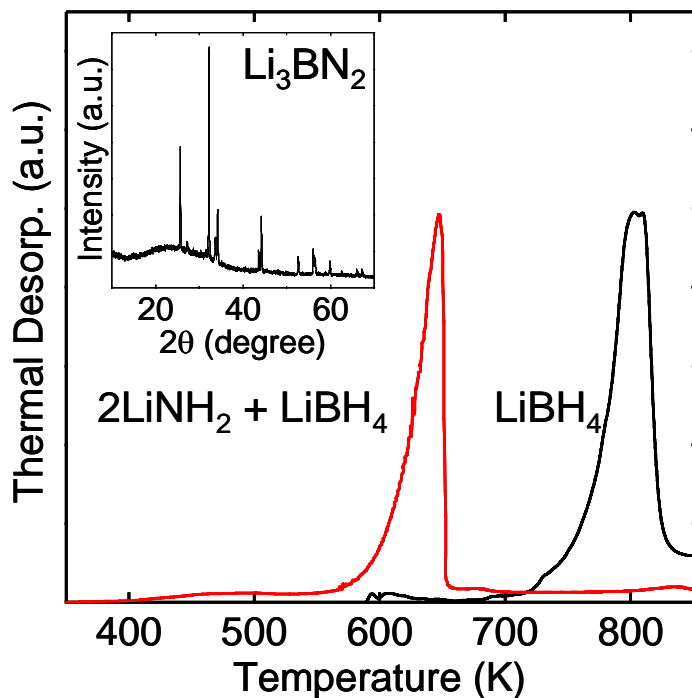
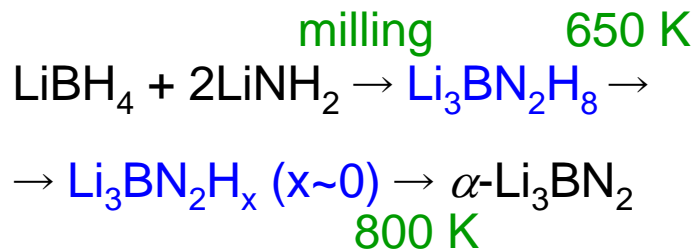


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*Any intermediate phase after/during dehydriding?*

- LiBH<sub>4</sub> + LiNH<sub>2</sub> : “Li-B-N(-H)” exists
- × LiBH<sub>4</sub> + LiAlH<sub>4</sub> : “Li-B-Al(-H)” may not exist

# Combination of $\text{LiBH}_4 + \text{LiNH}_2$



Y. Nakamori, A. Ninomiya, G. Kitahara, K. Aoki, T. Noritake, K. Miwa, Y. Kojima, S. Orimo, *J. Power Sources* in press

M. Aoki, K. Miwa, T. Noritake, G. Kitahara, Y. Nakamori, S. Orimo, S. Towata, *Appl. Phys. A* 80 (2005) 1409

# 4 Guidelines



---

1. Destabilization of  $\text{LiBH}_4$  and  $\text{LiNH}_2$   
*cation with larger electronegativity*
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3. Prevention of  $\text{NH}_3$ -contamination  
*“tunable” composition / starting material*
4. Provision of new reaction pathway  
*intermediate phase formed by dehydrating*

# Recent publications

## Theory

K. Miwa et al., "First principles study on lithium borohydride  $\text{LiBH}_4$ ", *Phys. Rev. B* 69 (2004) 245120

K. Miwa et al., "First-principles study on lithium amide for hydrogen storage", *Phys. Rev. B* 71 (2005) 195109

## Analysis

S. Orimo et al., "Material properties of  $\text{MBH}_4$  ( $M = \text{Li}, \text{Na}, \text{and K}$ )", *Mater. Sci. Eng. B* 108 (2004) 51

K. Ohoyama et al., "Revised crystal structure model of  $\text{Li}_2\text{NH}$  by neutron powder diffraction", *J. Phys. Soc. Jan.* 74 (2005) 483

T. Noritake et al., "Crystal structure and charge density analysis of  $\text{Li}_2\text{NH}$  by synchrotron X-ray diffraction", *J. Alloys Compd.* 393 (2005) 264

## Material Synthesis

Y. Nakamori, S. Orimo, "Destabilization of Li-based complex hydrides", *J. Alloys Compd.* 370 (2004) 271

S. Orimo et al., "Destabilization and enhanced dehydriding reaction of  $\text{LiNH}_2$  – an electronic structure viewpoint", *Appl. Phys. A (Rapid Commun.)* 79 (2004) 1765

Y. Nakamori, et al., "Synthesis and dehydriding studies of Mg-N-H systems", *J. Power Sources* 138 (2004) 309

M. Aoki et al., "Destabilization of  $\text{LiBH}_4$  by mixing with  $\text{LiNH}_2$ ", *Appl. Phys. A* 80 (2005) 1409.

Y. Nakamori et al., "Reversible hydrogen storage functions for the mixtures of  $\text{Li}_3\text{N}$  and  $\text{Mg}_3\text{N}_2$ ", *Appl. Phys. A* 80 (2005) 1

Y. Nakamori, et al., "Guidelines for developing amide based hydrogen storage materials", *Mater. Trans.*, in press

S. Orimo et al., "Dehydriding and rehydriding reactions of  $\text{LiBH}_4$ ", *J. Alloys Compd.* in press

Y. Nakamori et al., "Dehydriding reaction of mixed complex hydrides", *J. Power Sources*, in press