Synthesis and characterization of $Li_4(BH_4)(NH_2)_3$

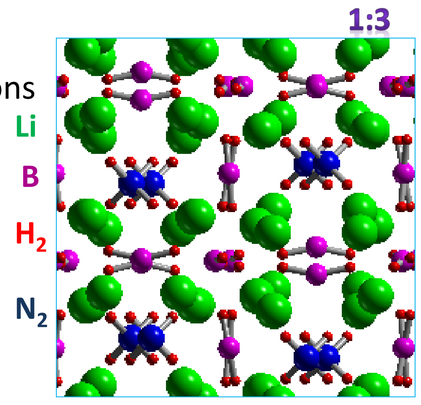
A. Wolczyk[a], A. Santoru[b], E. Marano[a], M. Chierotti[a], R.Gobetto[a], M. Baricco[a]
[a]Dipartimento di Chimica e Centro NIS, Università di Torino, V. Giuria 9, 10125, Torino, Italy
[b]Helmholtz-Zentrum Geesthacht GmbH, Institute of Materials Research, Max-Planck-Strasse 1,D-21502 Geesthacht, Germany
Email: annaroza.wolczyk@unito.it

Motivation + Goal

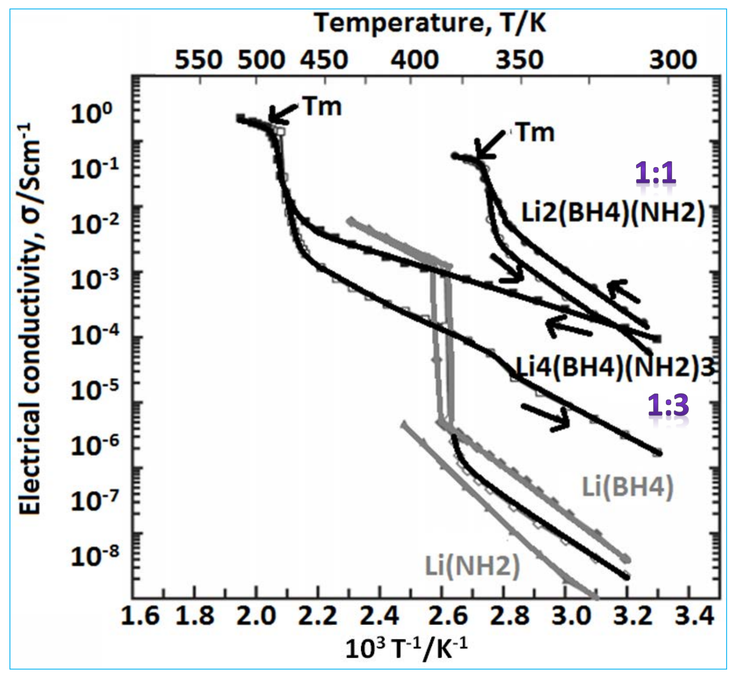
$LiBH_4$ mix with $LiNH_2$
1:3 $Li_4(BH_4)(NH_2)_3$

Main goal
- Hydrogen storage
- batteries

- Comparision of different synthesis to obtain this specific compound 1:3
- $Li_4BN_3H_{10}$ is of great interest for hydrogen storage and for lithium-ion battery solid electrolytes because of its high hydrogen content and high lithium-ion conductivity, respectively. The practical hydrogen storage application of this complex hydride is, however, limited due to irreversibility and cogeneration of ammonia (NH_3) during the decomposition
- The development of lithium ion conductors is important because of their potential applications as solid electrolytes for lithium ion batteries.



Materials Transactions, Vol. 52, No. 4 (2011) pp. 654-657 Y. Zhou, M. Matsuo, Y. Miura, H. Takamura, H. Maekawa,A. Remhof, A. Borgschulte, A. Zuttel, T. Otomo and Orimo



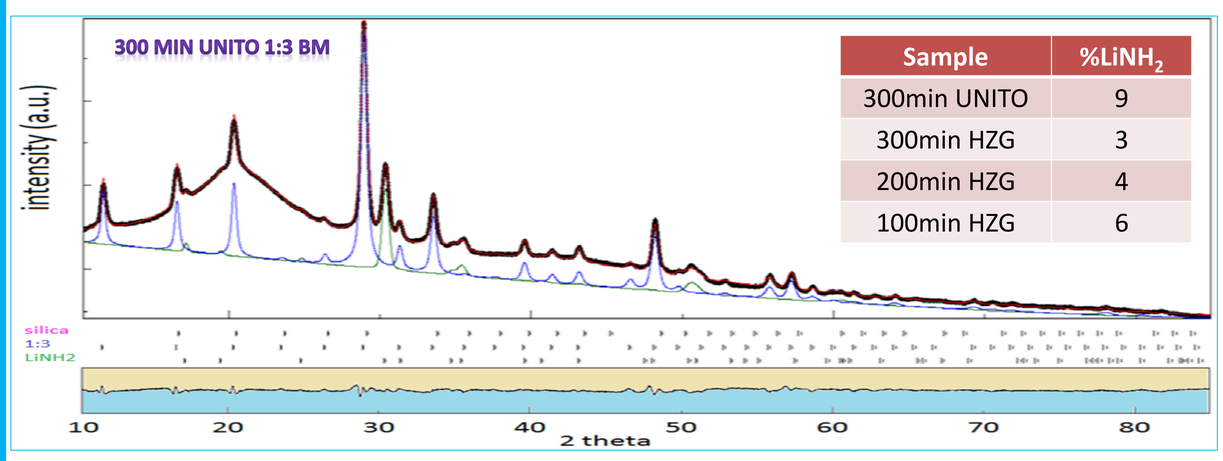
Synthesis

- Ball milling (BPR:10, BPR:14, t=100÷300min)
- Thermal treatment (100°C, 120°C,250°C)

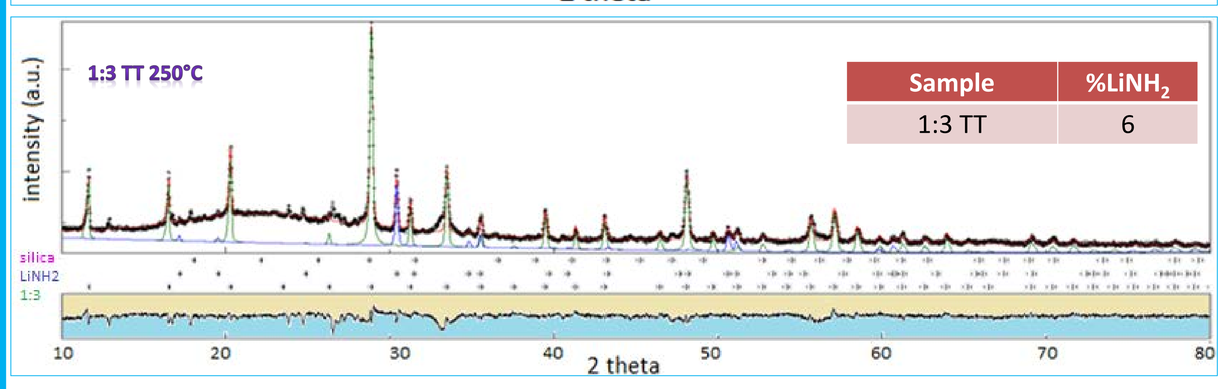
Techniques

- XRD (diffractometer system PW3040/60 X'Pert PRO MPD from PANalytical. The source: high power ceramic tube PW3373/10 LFF, Cu anode)
- HP-DSC (DSC 204 HP Phoenix® – High-pressure DSC)
- ssNMR (System: Bruker AVANCE II 400, Magnet: Bruker Ultrashield ™ 400 PLUS, Probe: Tuneable Multinuclear Probes)

XRD Refinement



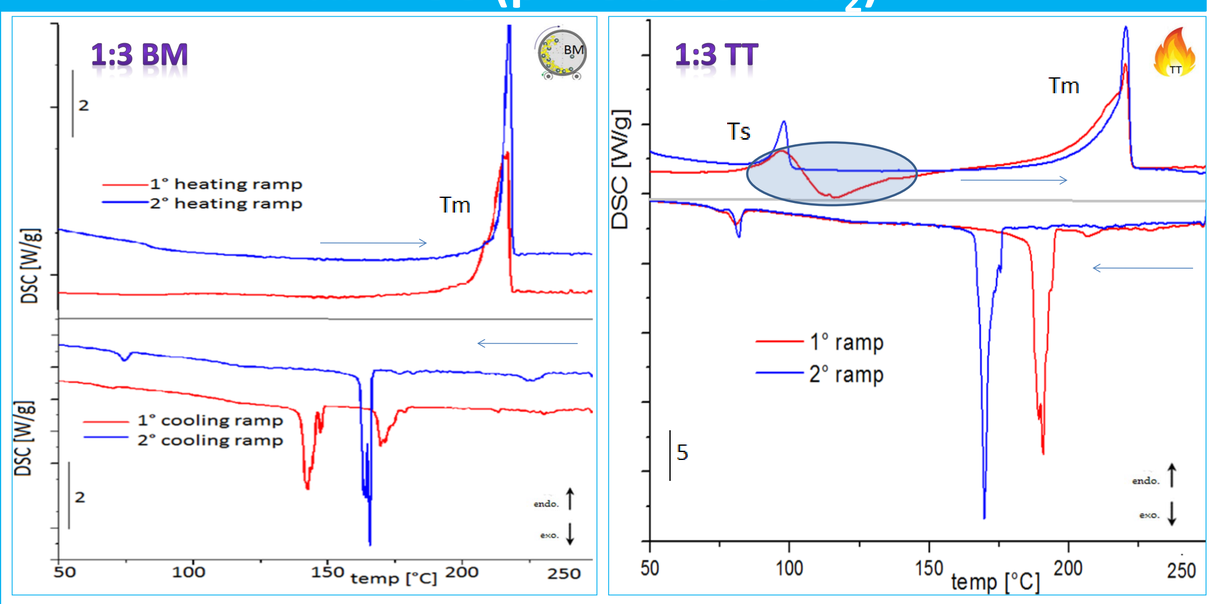
Sample	%$LiNH_2$
300min UNITO	9
300min HZG	3
200min HZG	4
100min HZG	6



Sample	%$LiNH_2$
1:3 TT	6

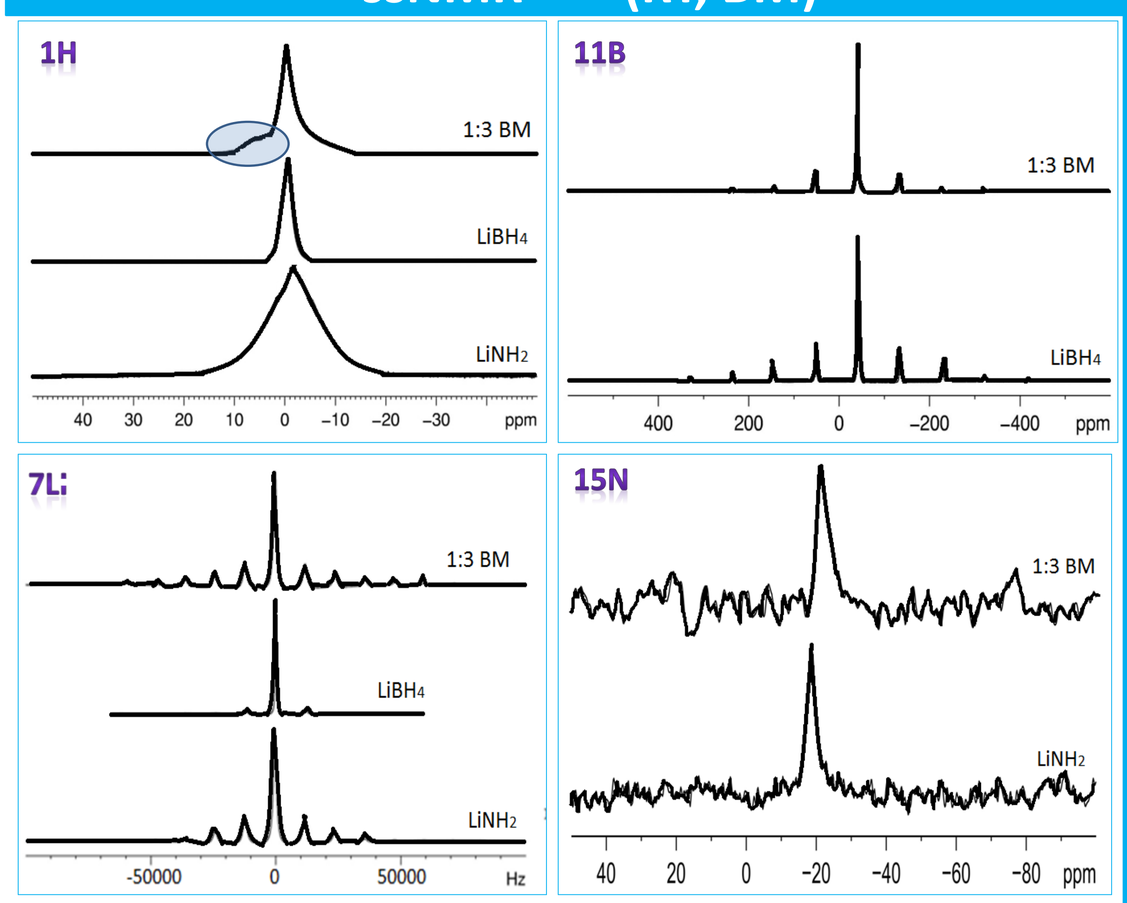
- constant control of phases to obtain pure 1:3 compound

HP-DSC (p=10 bars of H_2)



- calculations of different ΔH values, for melting and formation changes

ssNMR (RT, BM)

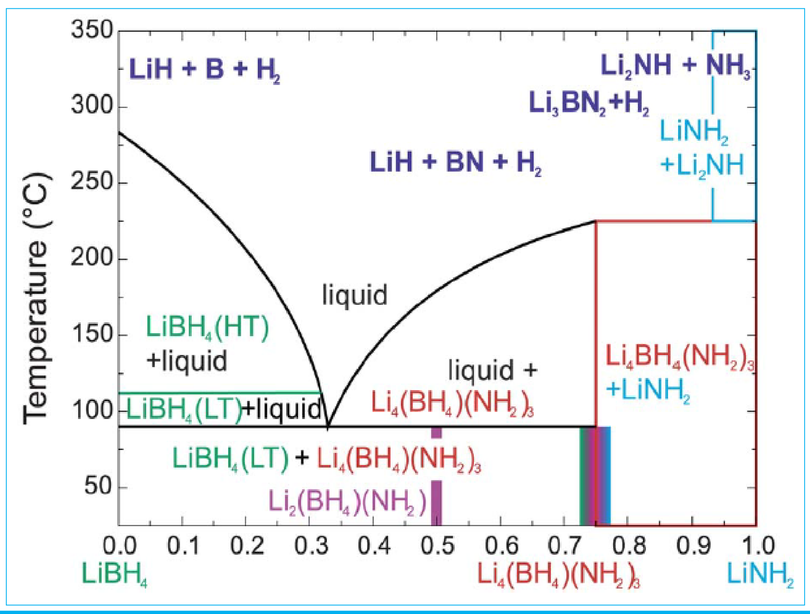


- **peaks can become wider because of**
1. static (site dispersion) or dynamic (mobility) disorder
2. residual dipolar coupling (if covalently bonded to quadrupolar nuclei)
- **NMR spectra analyze**
1. position of central peak (chemical shift)
2. pattern of spinning sidebands

Conclusions + Future plans

- H_2 delivering in lower temperature?
- role of pure **$LiNH_2$**!?
- ternary system (+LiI?)
- **DSC** for greater ratio variations (e.g. 0.33)
- **TT** in agreement with **BM**
- heating influence in **NMR**
- Pseudo-binary **phase diagram**

Energy Environ. Sci., 2012, 5, 6823 A. Borgschulte,M. O. Jones, E. Callini, B. Probst, S.Kato, A. Zuttel, W. I. F. Davidb and Orimo



The research leading to these results has received funding from the People Program (Marie Curie Actions) of the European Union's Seventh Framework Program FP7/2007-2013/ under REA grant agreement n° 607040 (Marie Curie ITN ECOSTORE) is thankfully acknowledg