Multifunctionality of metal hydrides for energy storage – developments and perspectives

18th-21st September - Warsaw University of Technology - POLAND

Aluminum Chloride as effective dopant in Amide-based systems

Dr. Sebastiano Garroni

UNIVERSIDAD DE BURGOS

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MARIE CURIE ACTIONS

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Dr. Santiago Cuesta-Lopez

What is ICCRAM?

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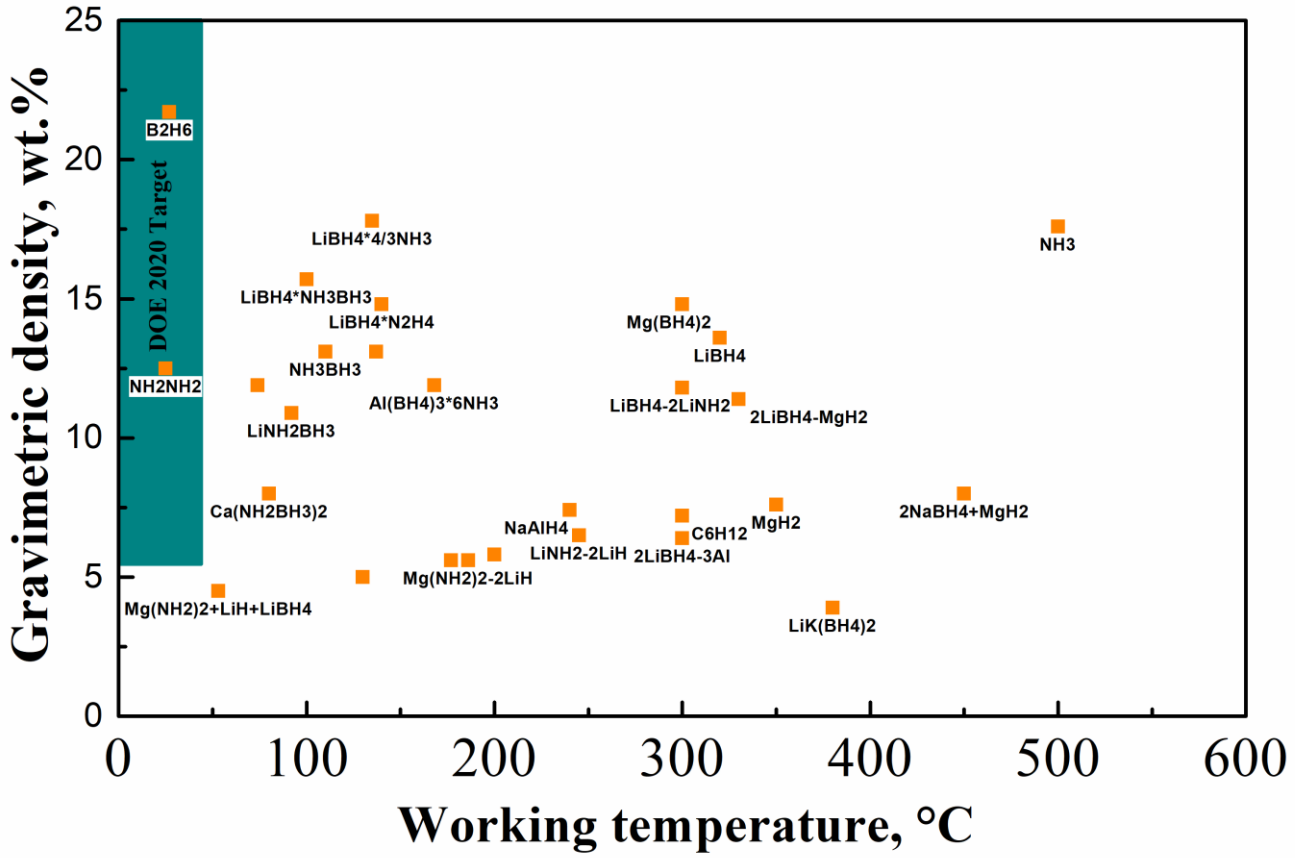
Materials for hydrogen storage 2007-2017



[1] Chen P. et al., Nature Reviews Materials 1, 16059 (2016).
[2] T.R. Jensen et al., Chem. Soc. Rev., 2017,46, 1565-1634.
[3] H. Wang, G. Wu, H. Cao, C. Pistidda, A.-L. Chaudhary, S. Garroni, M. Dornheim, and P. Chen, Adv. Energy Mater. 2017, 7, 1602456

Materials for hydrogen storage: M-N-H

$$LiNH_2(s) + LiH(s) <-> Li_2NH(s) + H_2(g)$$

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Advantages:

- Good gravimetric capacity (6.5 wt. %)
- Good reversibility (Pressure < 5.0 MPa; Temperature ~ 300 °C)
- Promising thermodynamic properties (calculated: -44.5 kJ/mol H_2; experimental: 66 kJ/mol H_2)

Disadvantages:

- Slow desorption kinetic
- Release of NH_3

Strategies:

- Particle size reduction by ball milling.
- Nanoconfinement
- Addition of Metal Halide

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- **$AlCl_3$**

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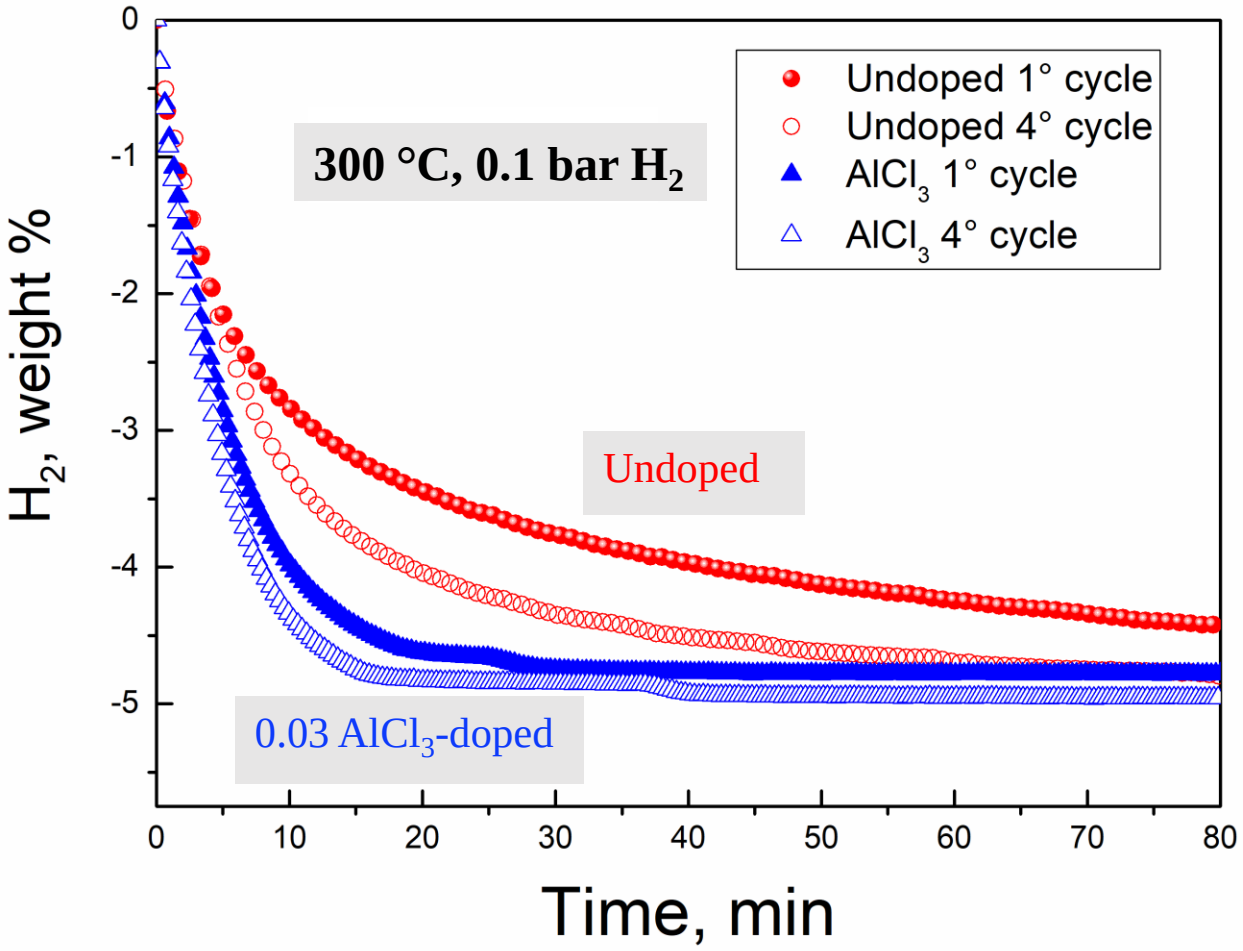
Effect of $AlCl_3$ on the $LiNH_2$ + LiH system



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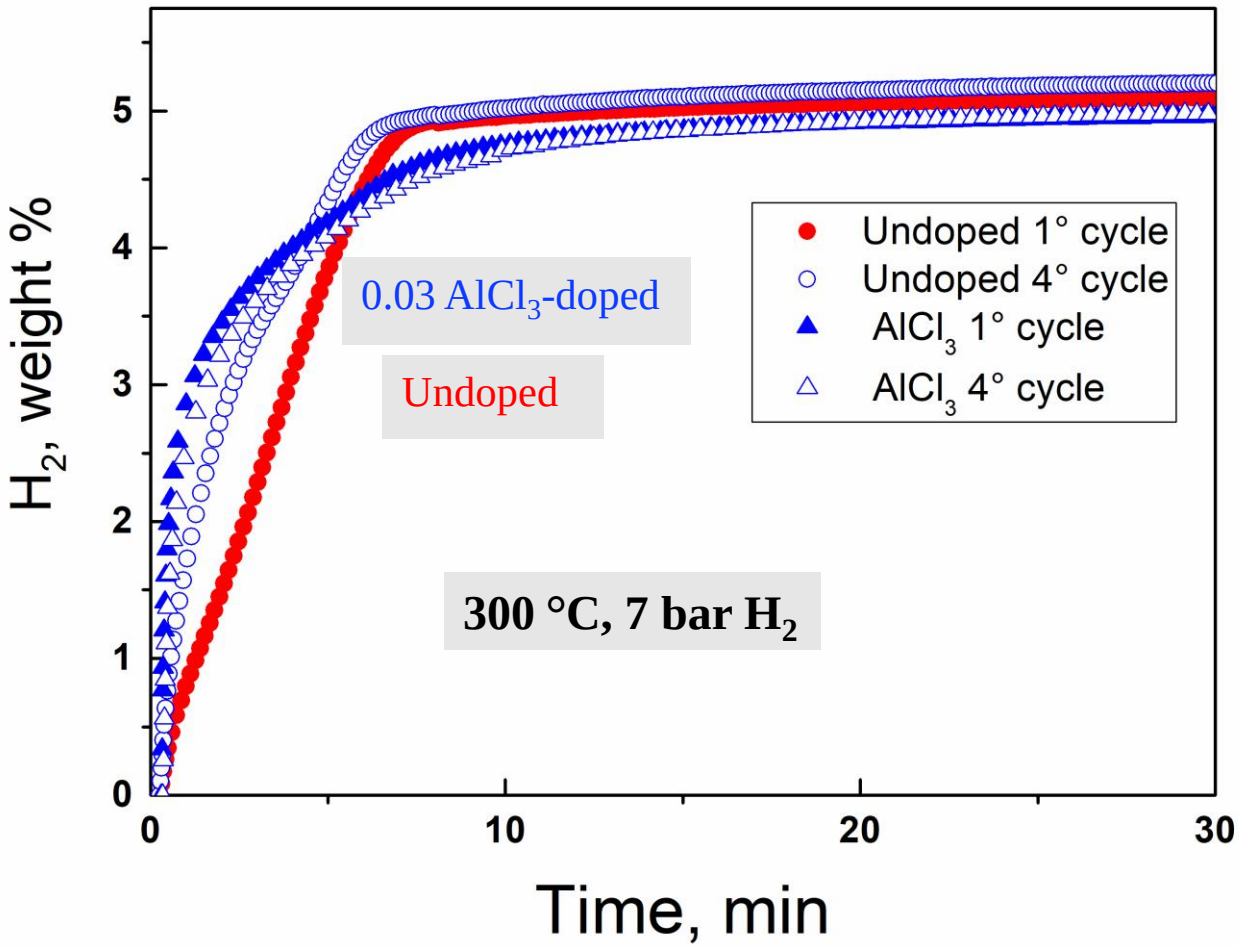

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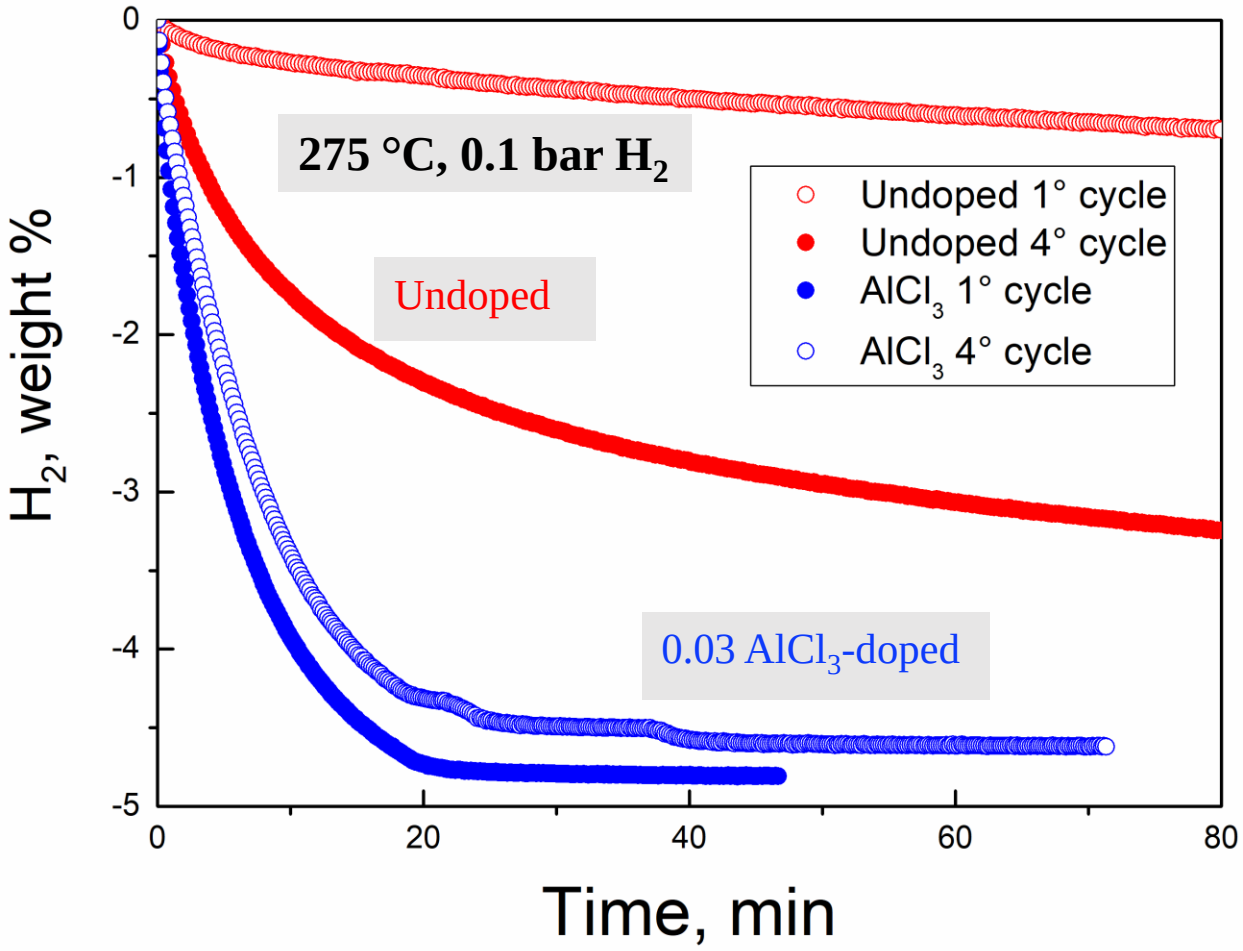

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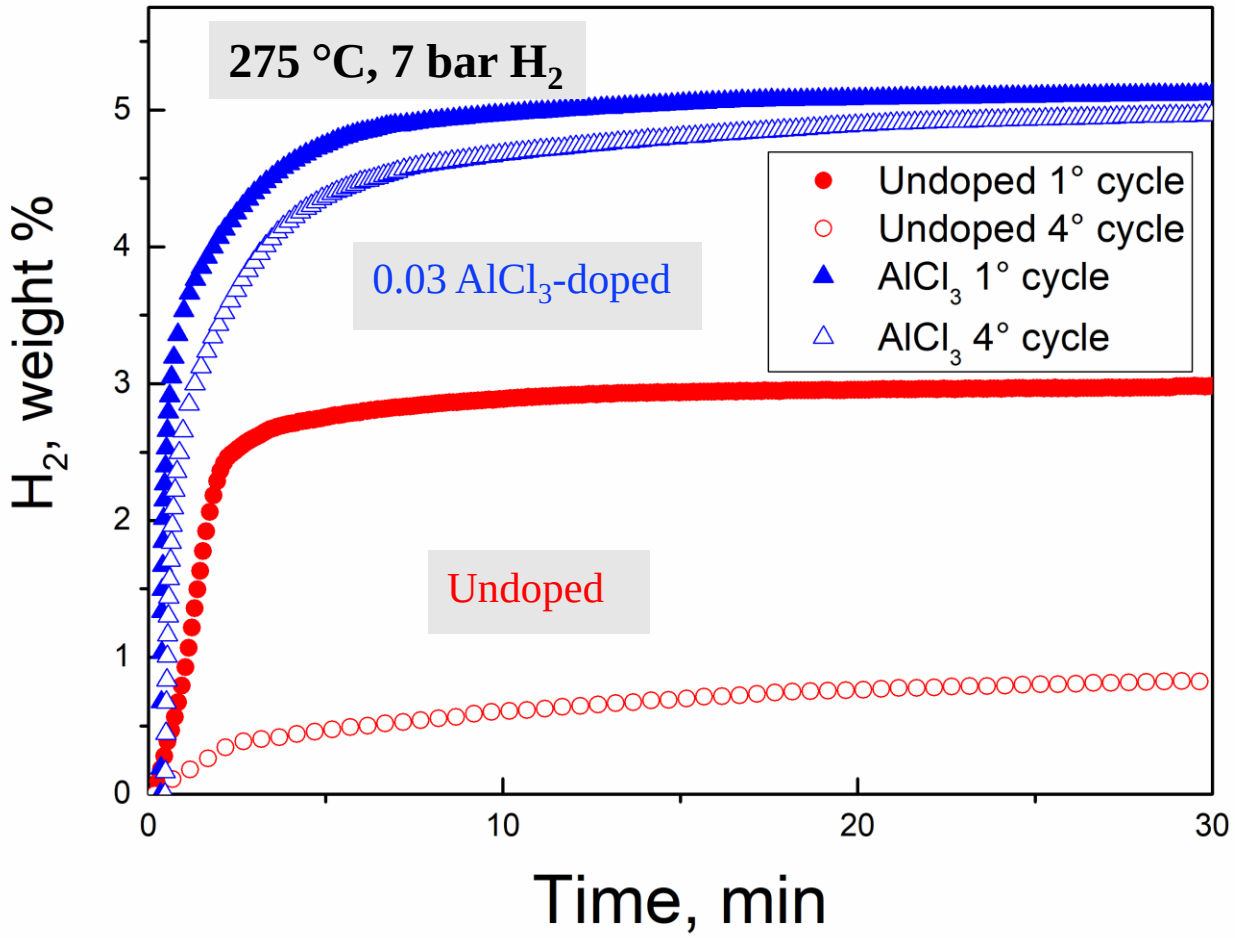

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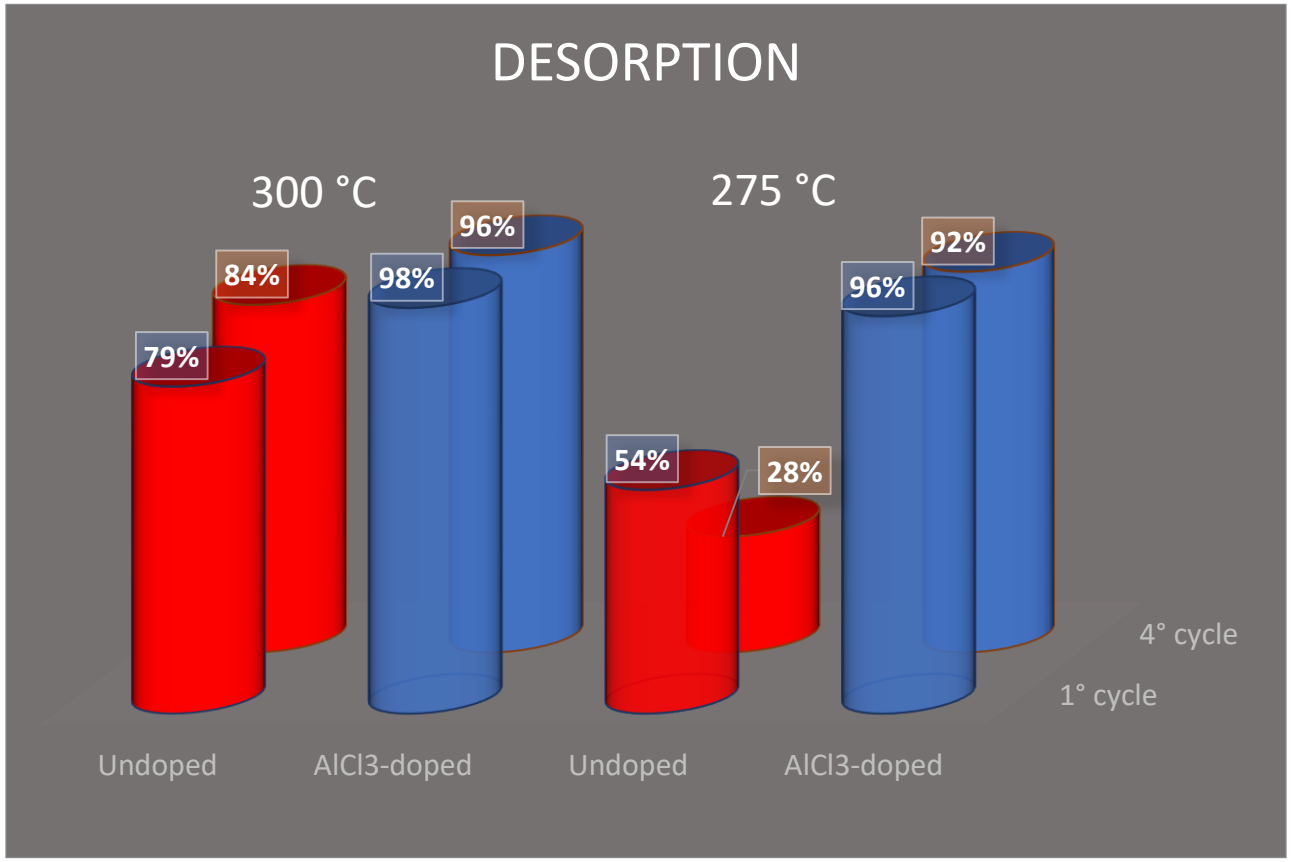
Cyclability



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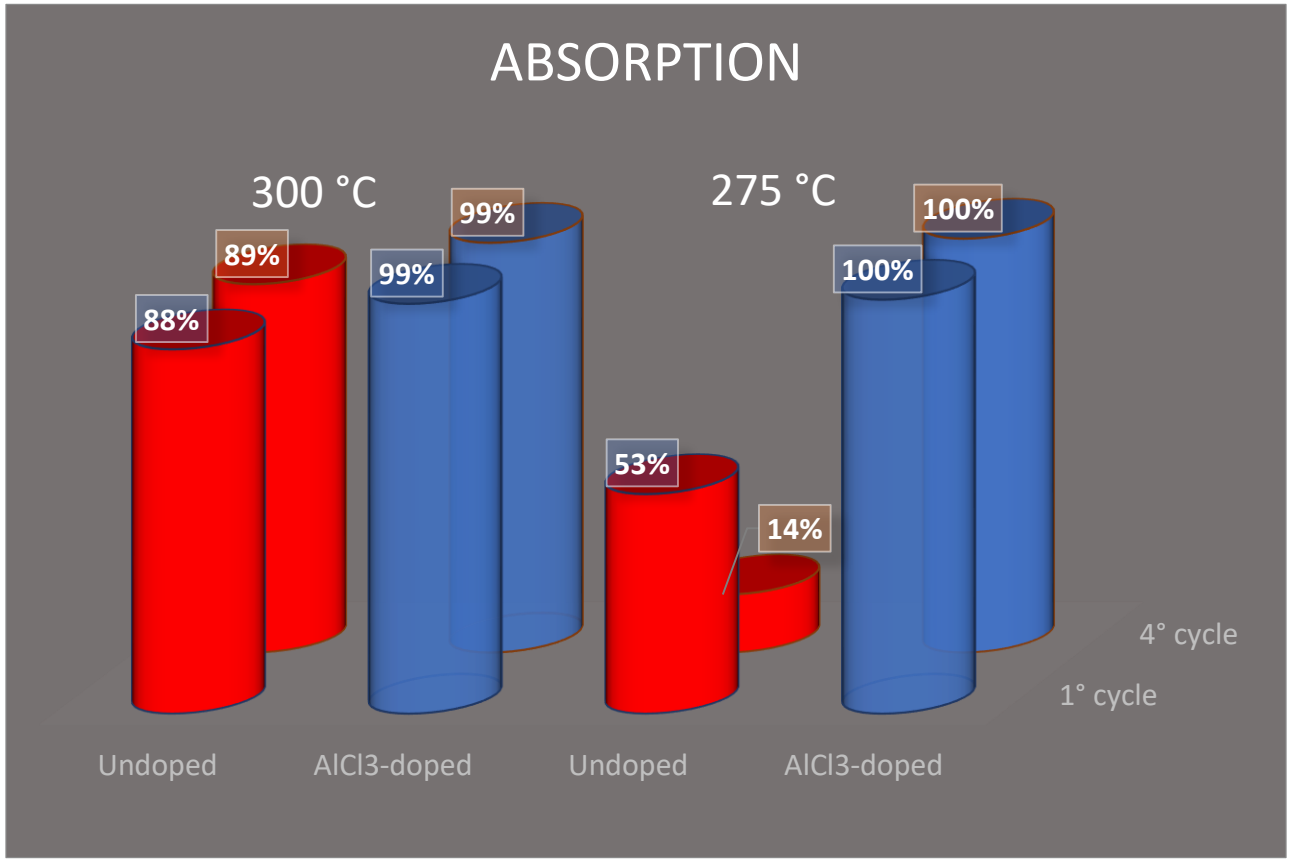

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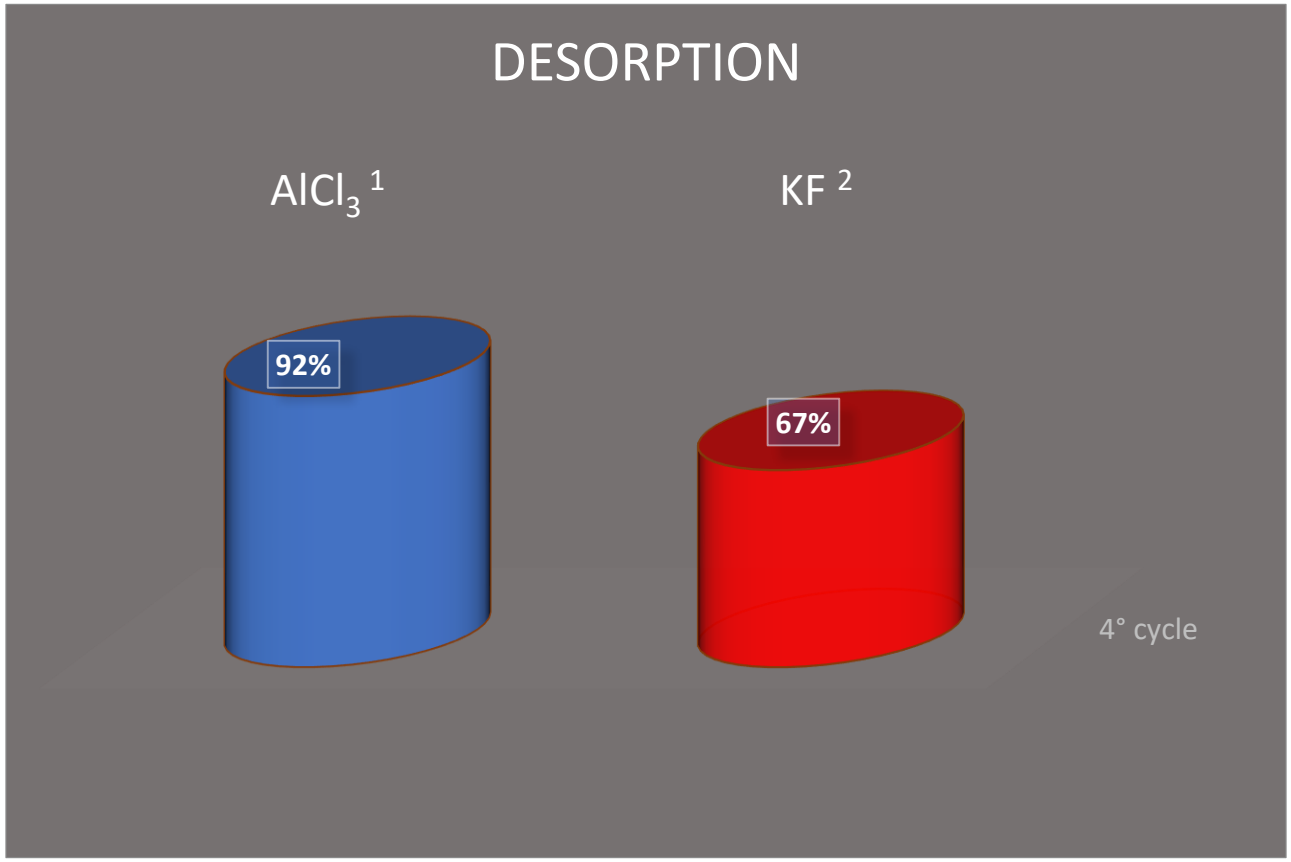
Cyclability – comparison with KF



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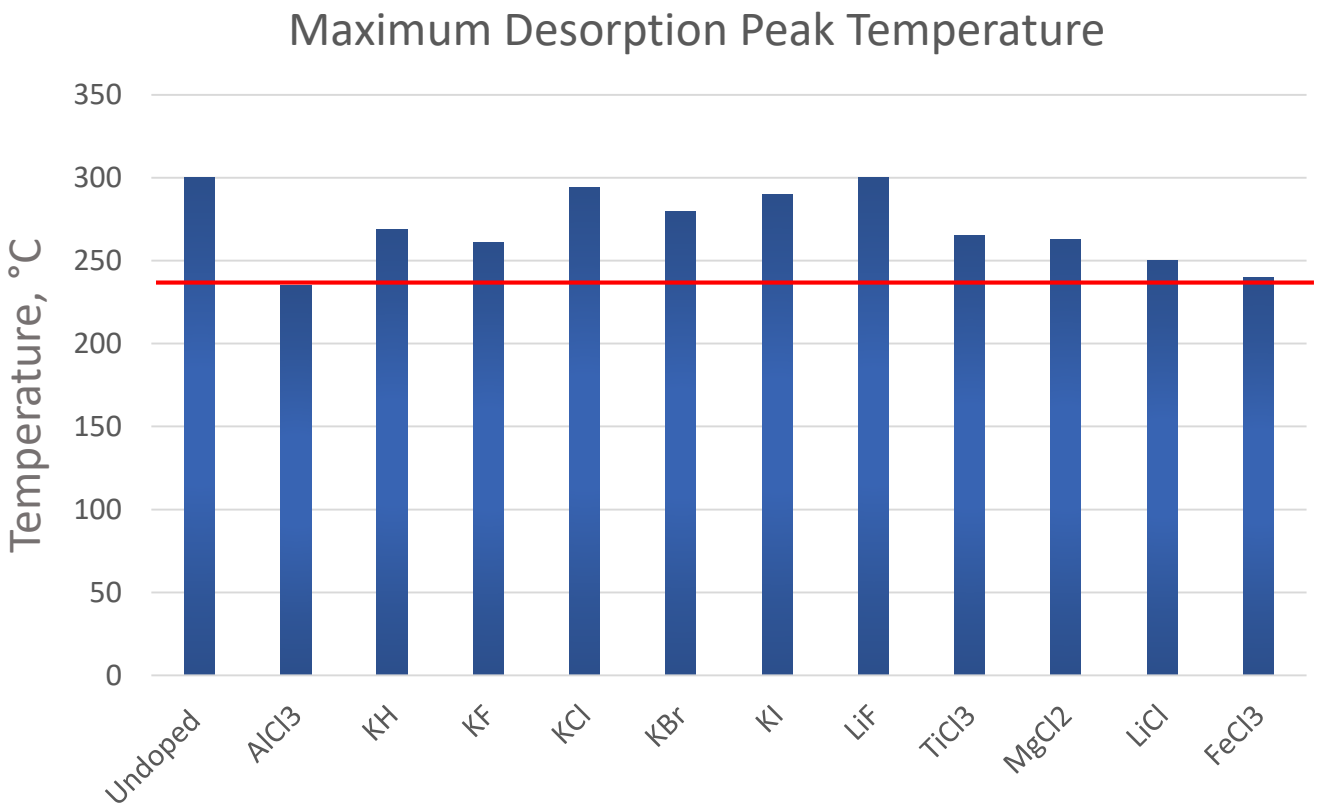
[2] Y.L. Teng et al., In J. Hydrogen Energy,2016, 41, 16122.

Desorption temperatures – other additives



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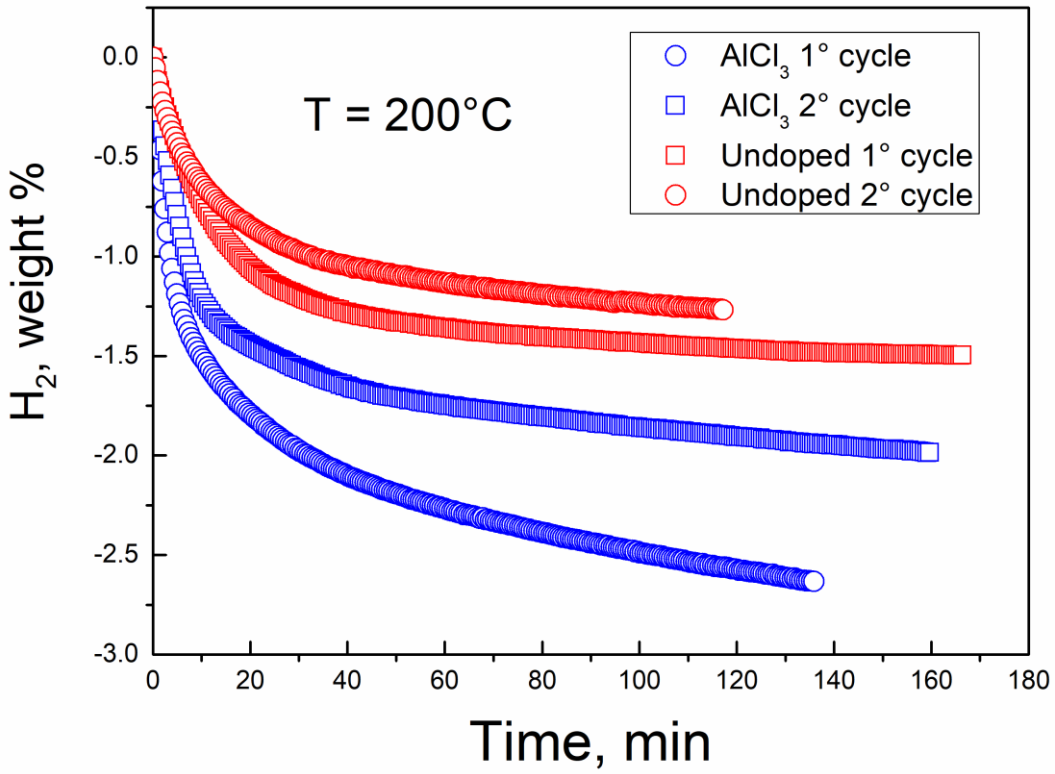
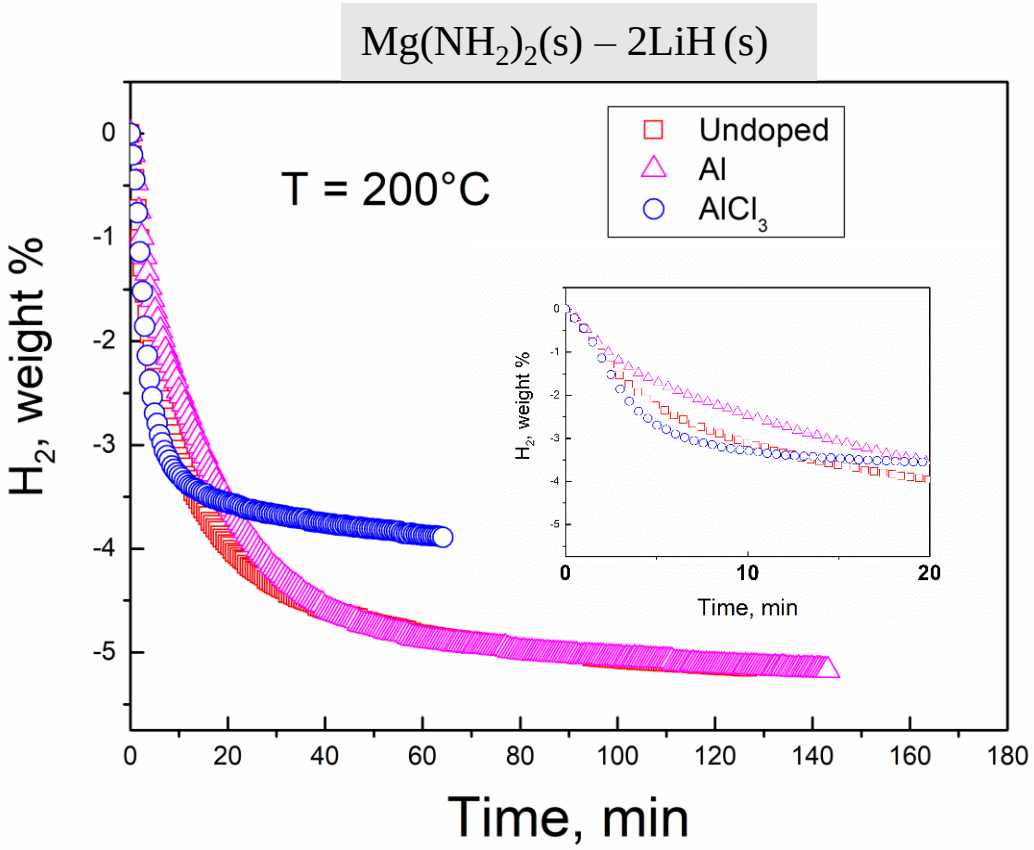
[3] G. Wu et al., Progress in Natural Science: Materials International , 2017, 27, 139.

$2LiNH_2(s) – MgH_2(s)$ system



S. Garroni. **Aluminum Chloride as effective dopant in Amide-based systems**

$Mg(NH_2)_2(s) – 2LiH\,(s)$ system



S. Garroni. **Aluminum Chloride as effective dopant in Amide-based systems**

Structural Investigation

$LiNH_2(s) + 1.6LiH(s) + 0.03AlCl_3$

- Initial mixture: hand mix of the starting reagents
- Ball milled for 5 hours
- Annealing at different temperatures

Goal:

- Which is the active phase?

Characterization:

- XRD
- FT-IR
- MAS NMR

[1] Fernandez Albanesi L, Garroni S., Arneodo Lorochette P, Nolis, P., Mulas G., Enzo S., Barò M.D., Gennari FC. Int J Hydrogen Energy 2015;40,:13506-17.

Structural Investigation: XRD

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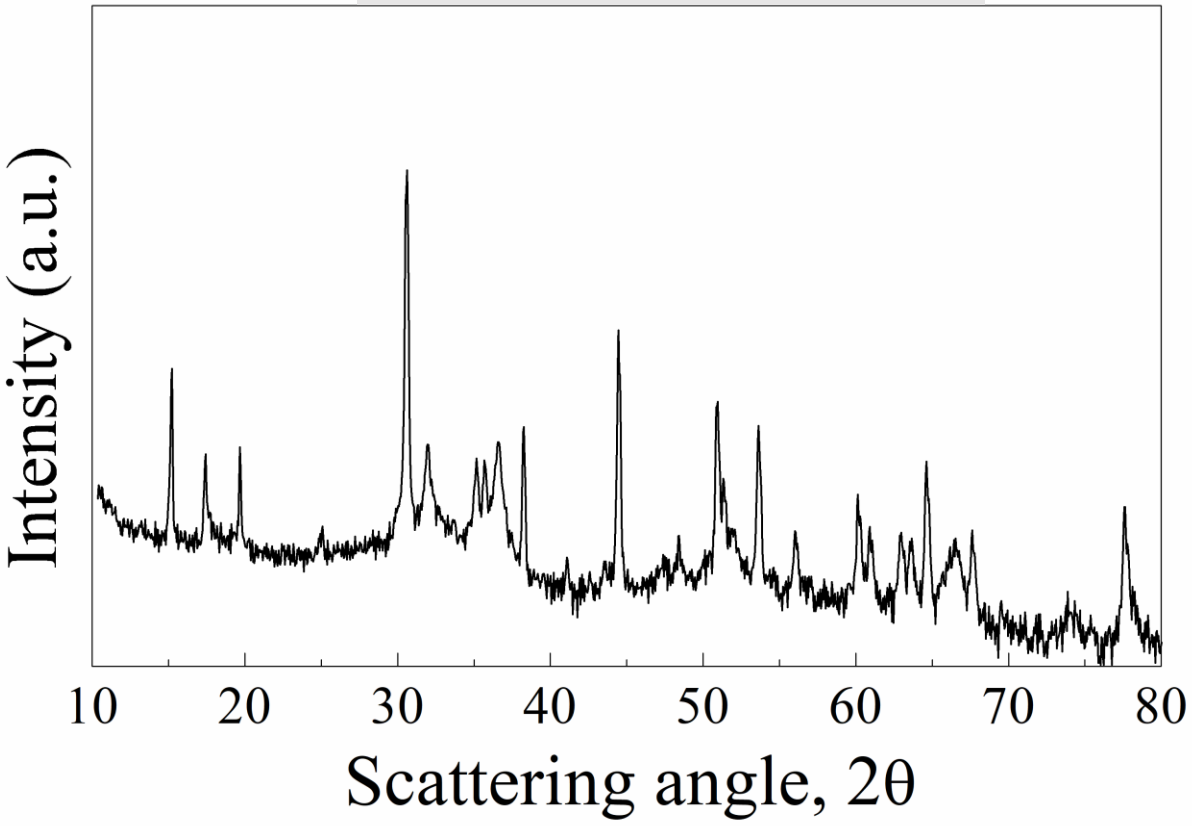

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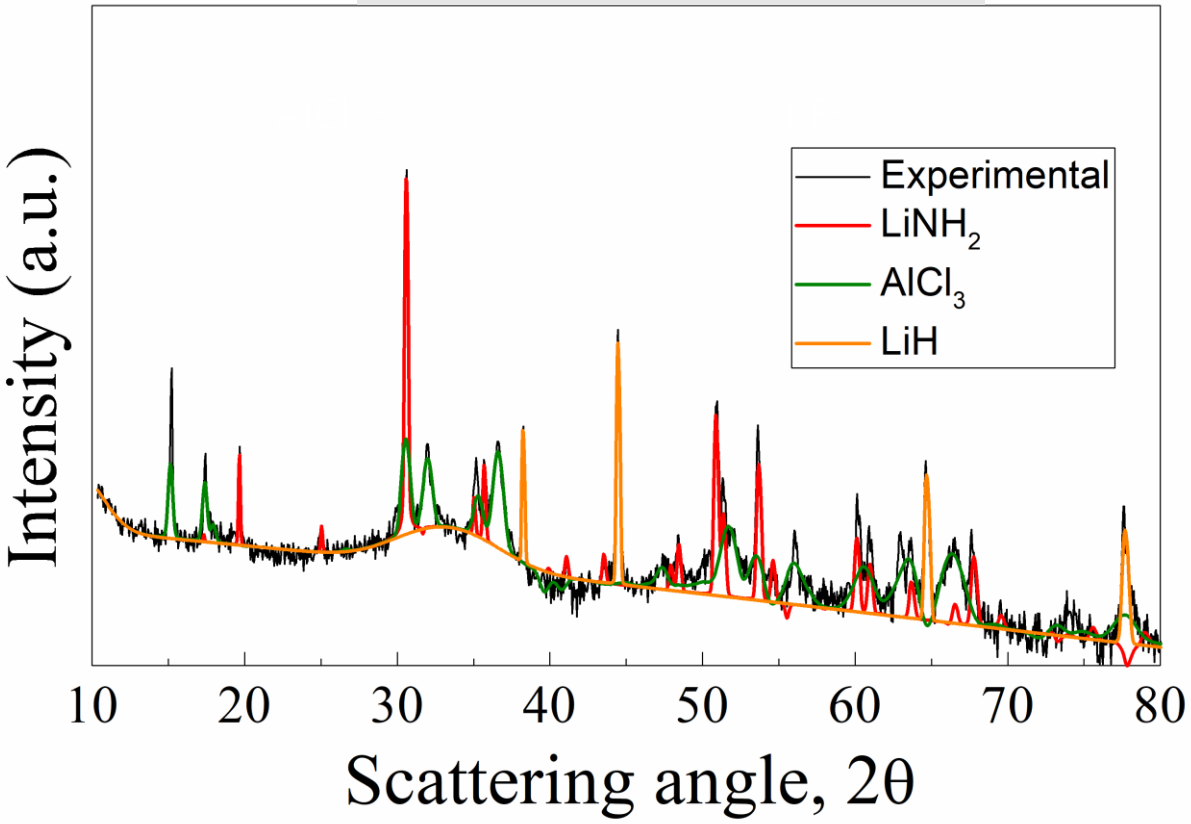

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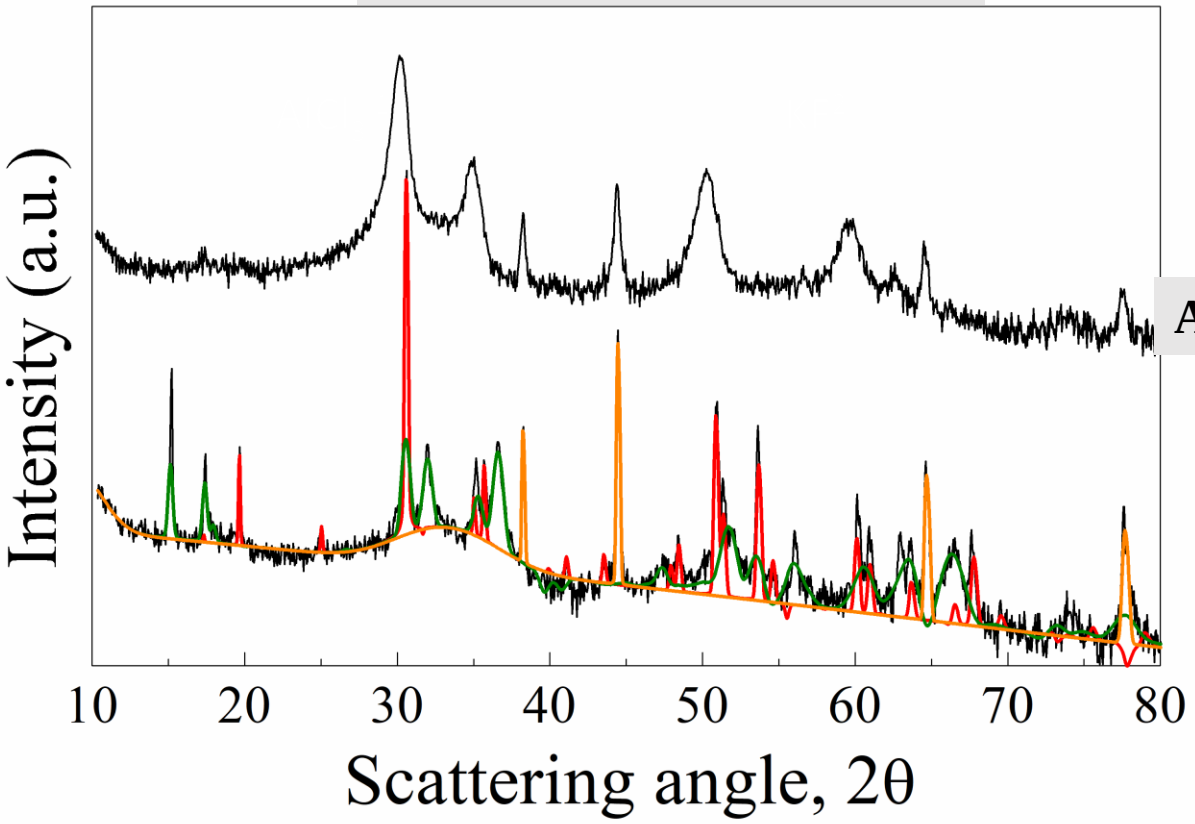

After 5h ball milling

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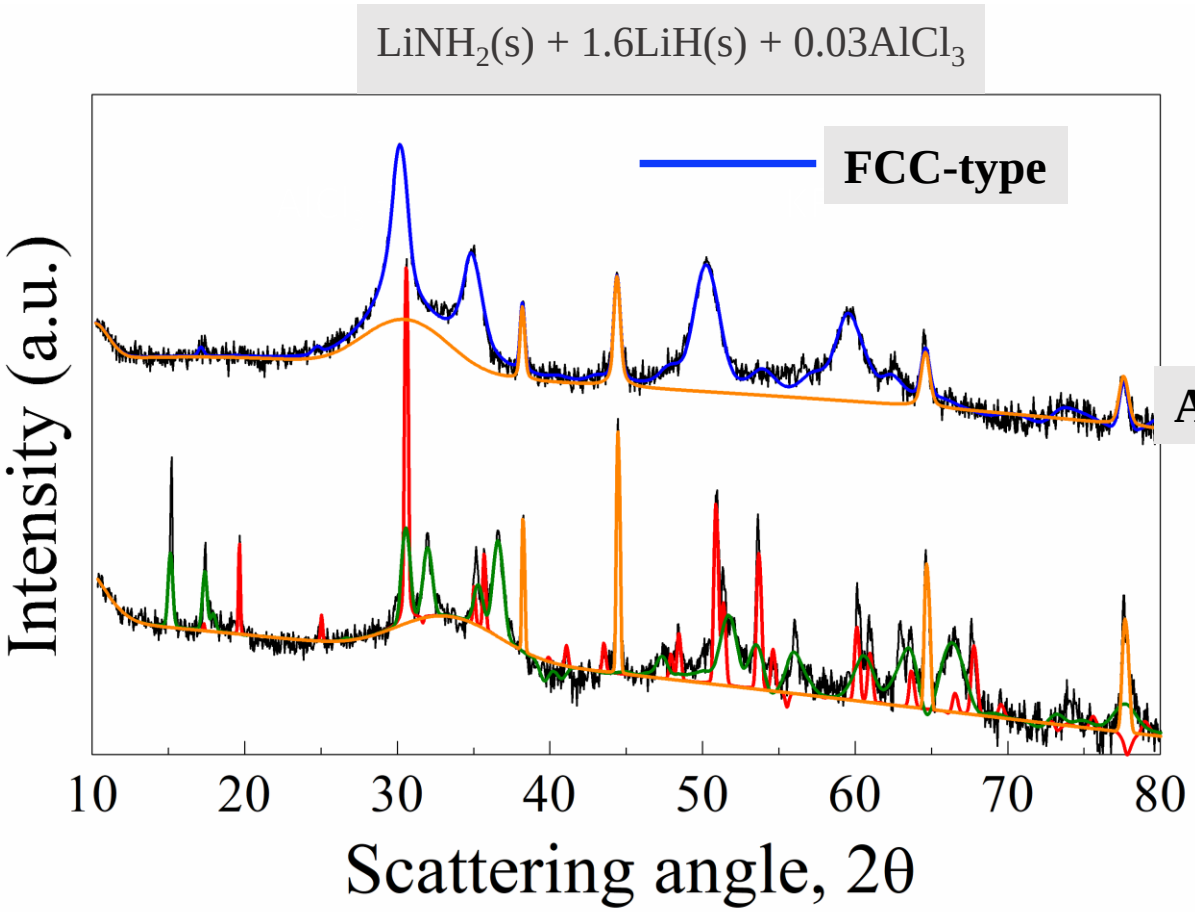

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Structural Investigation: FT-IR

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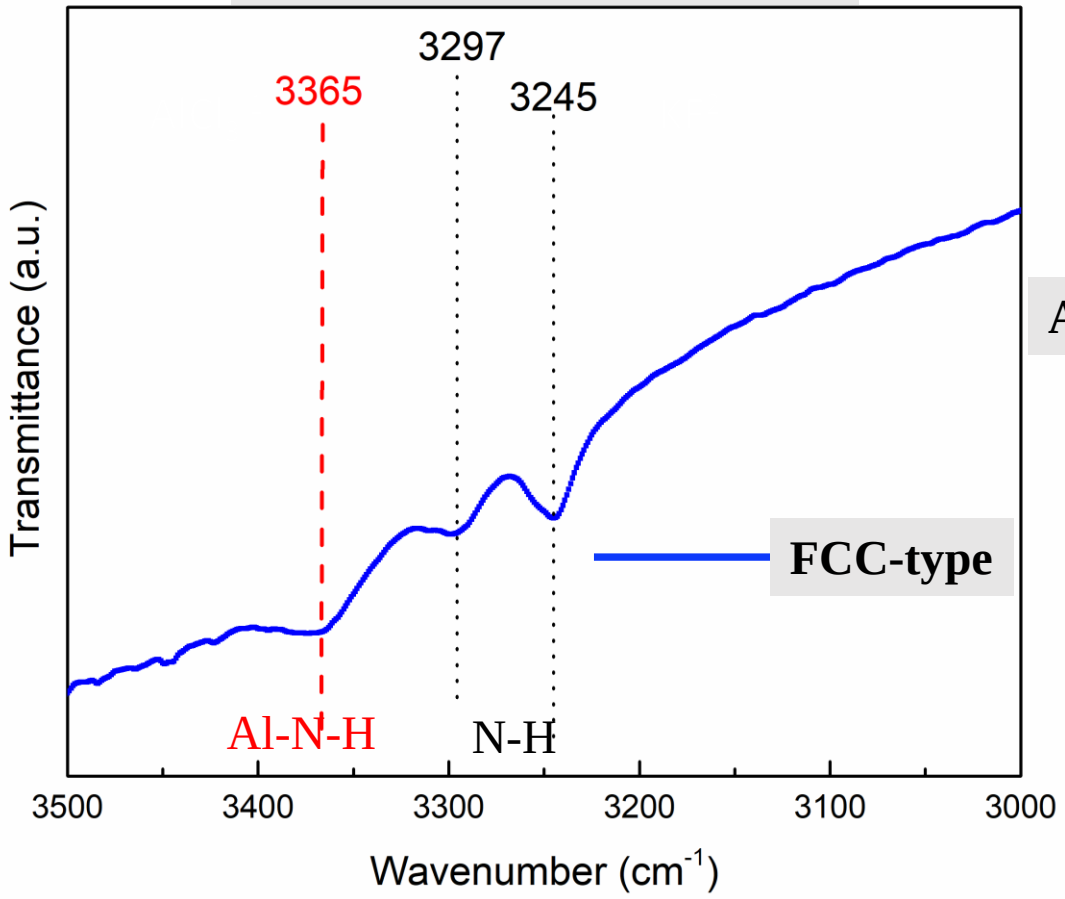

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Structural Investigation: MAS NMR

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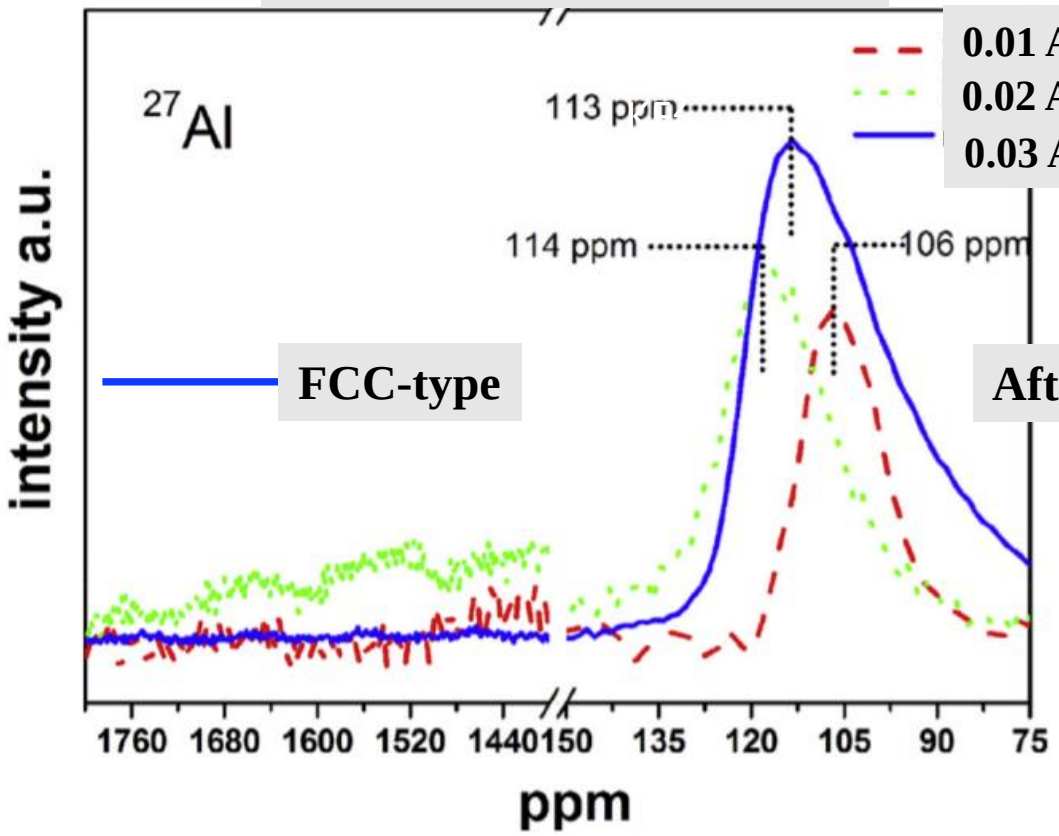

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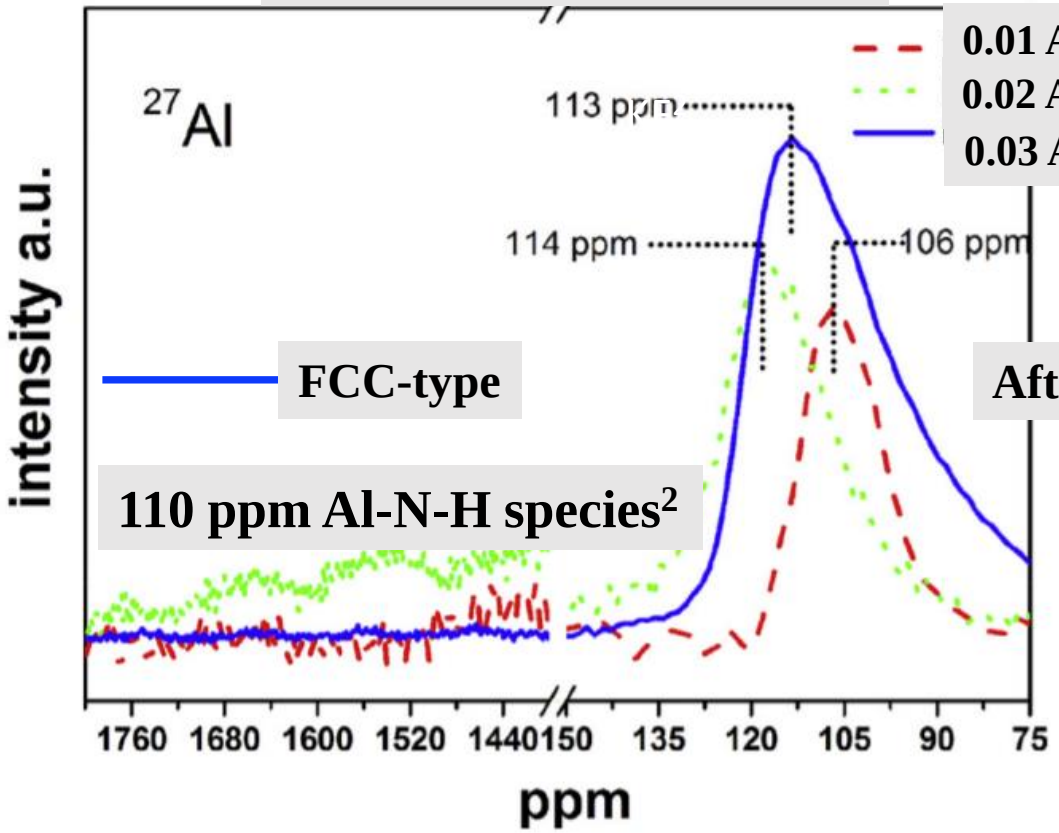

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Structural Investigation: Upon annealing - XRD

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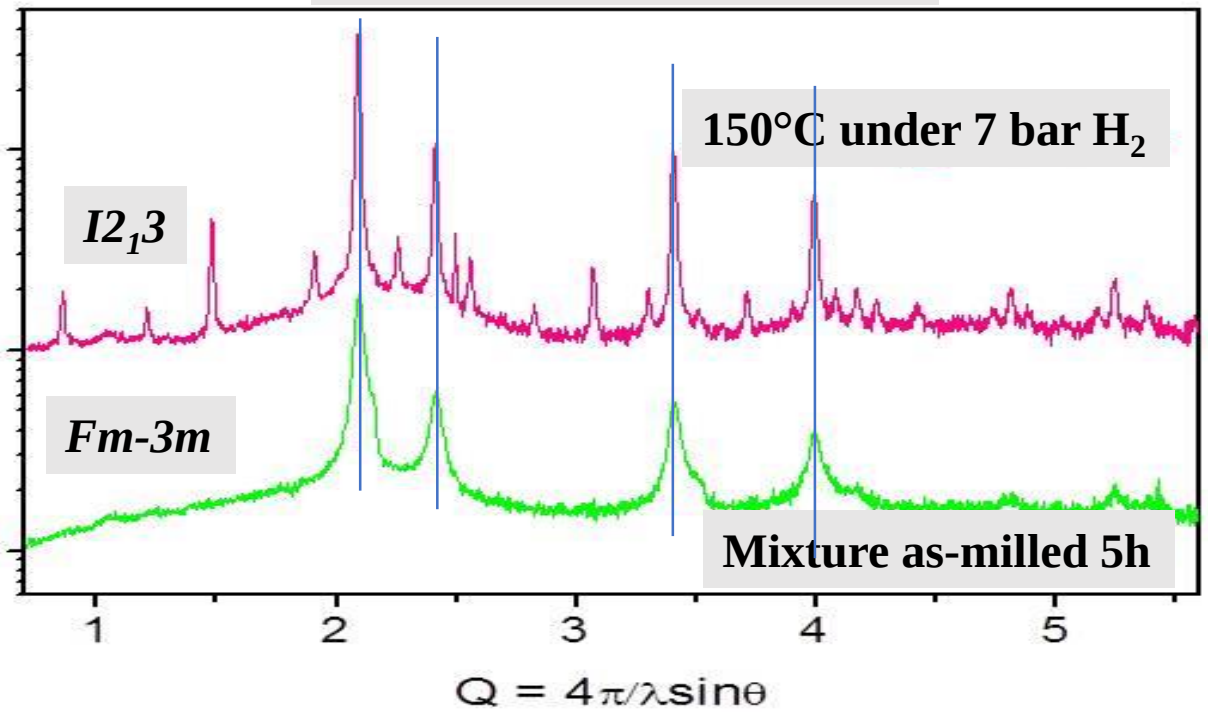

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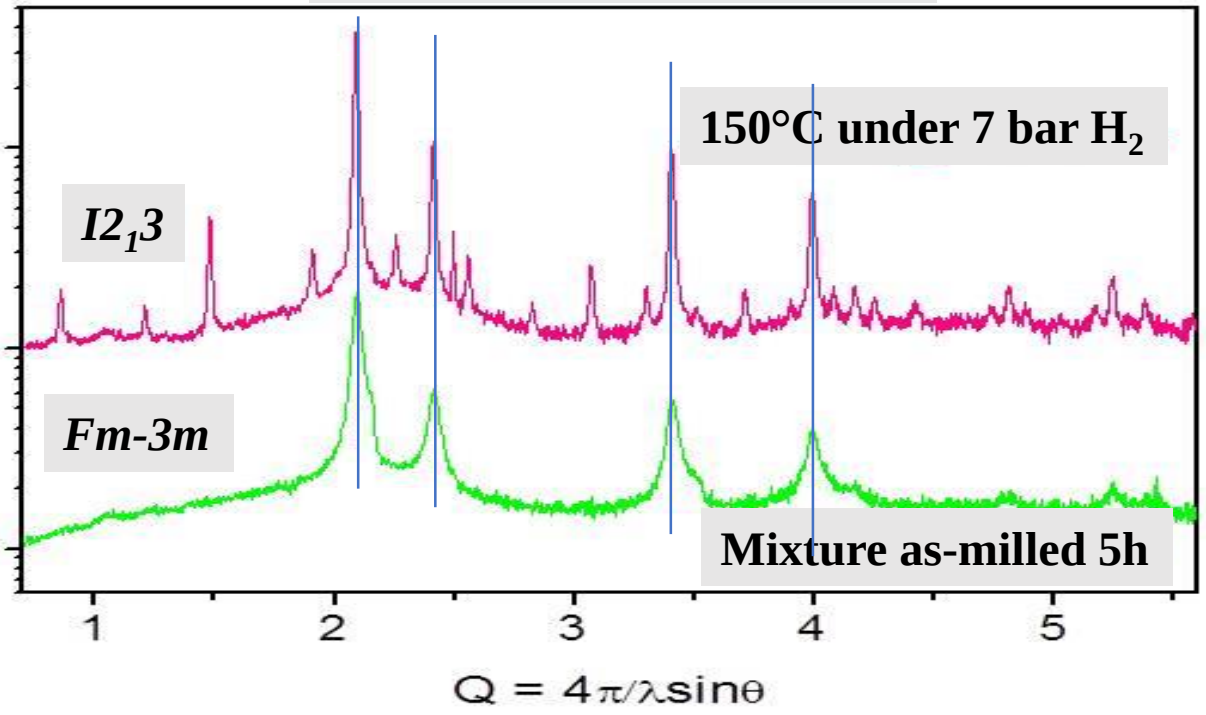

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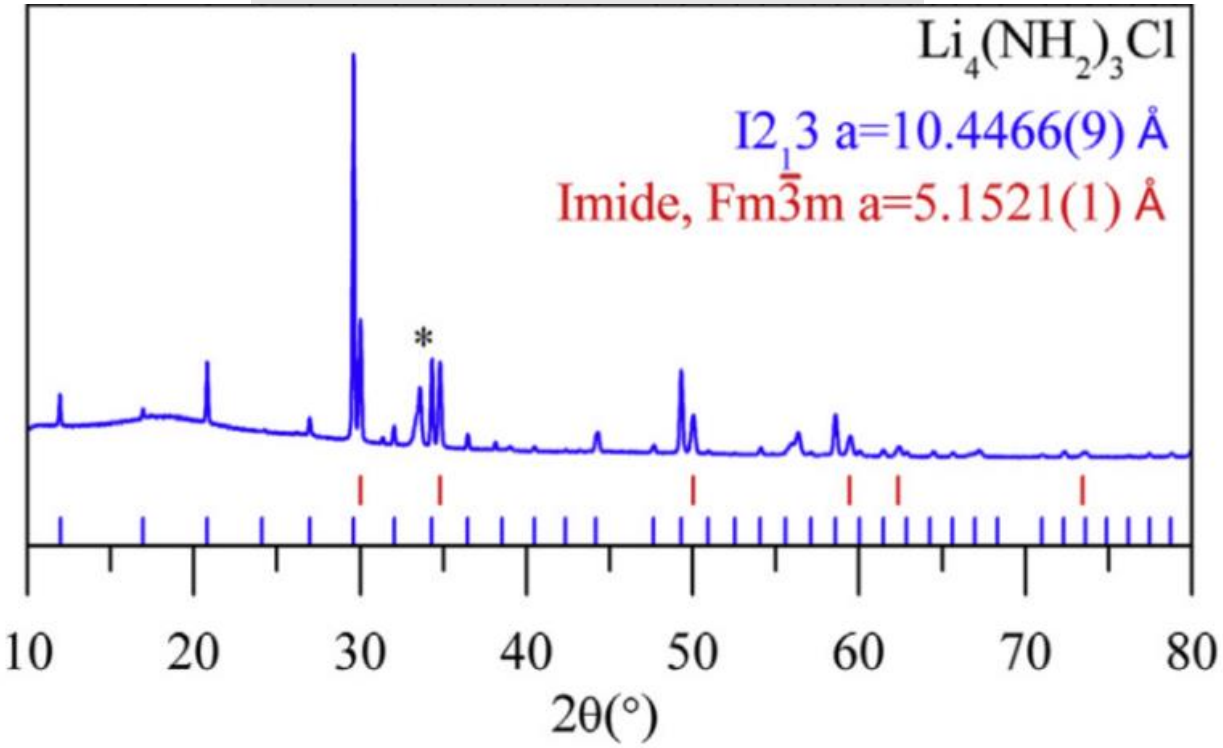
Structural Investigation: Upon annealing - XRD

Synthesis and characterization of two new amide chloride compounds: Potential H_2 storage materials

Rosalind A. Davies [a,b], *Paul A. Anderson* [a,*]

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 40 (2015) 3001–3005

Reaction between $LiNH_2$+LiCl



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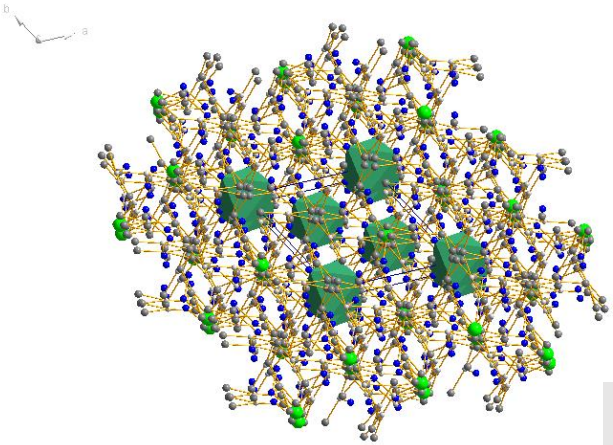

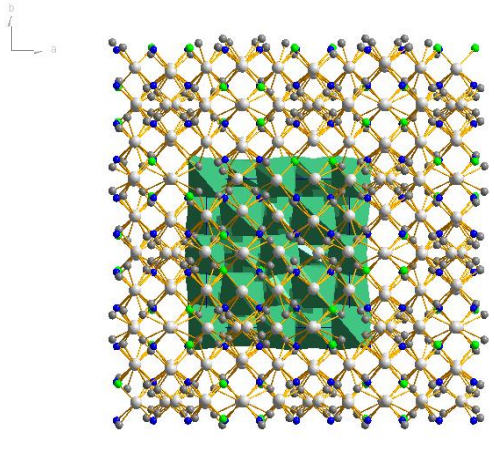

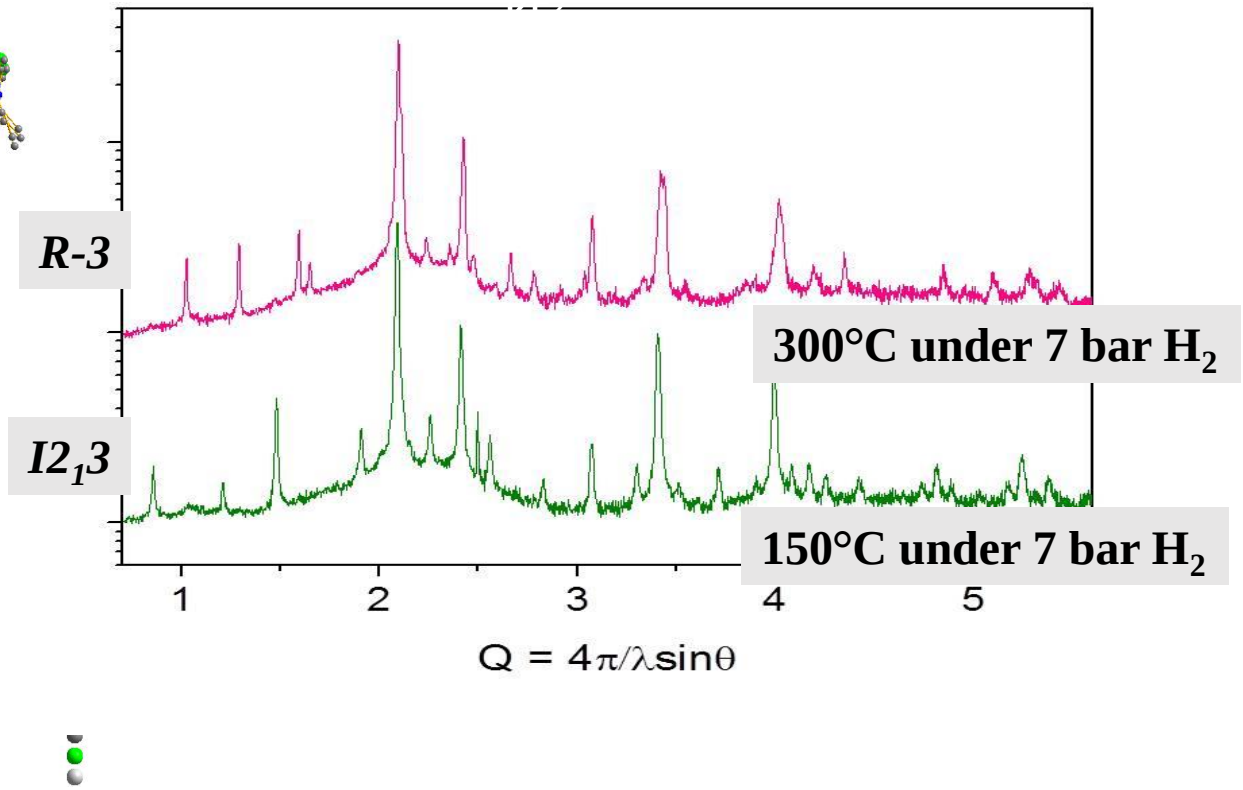

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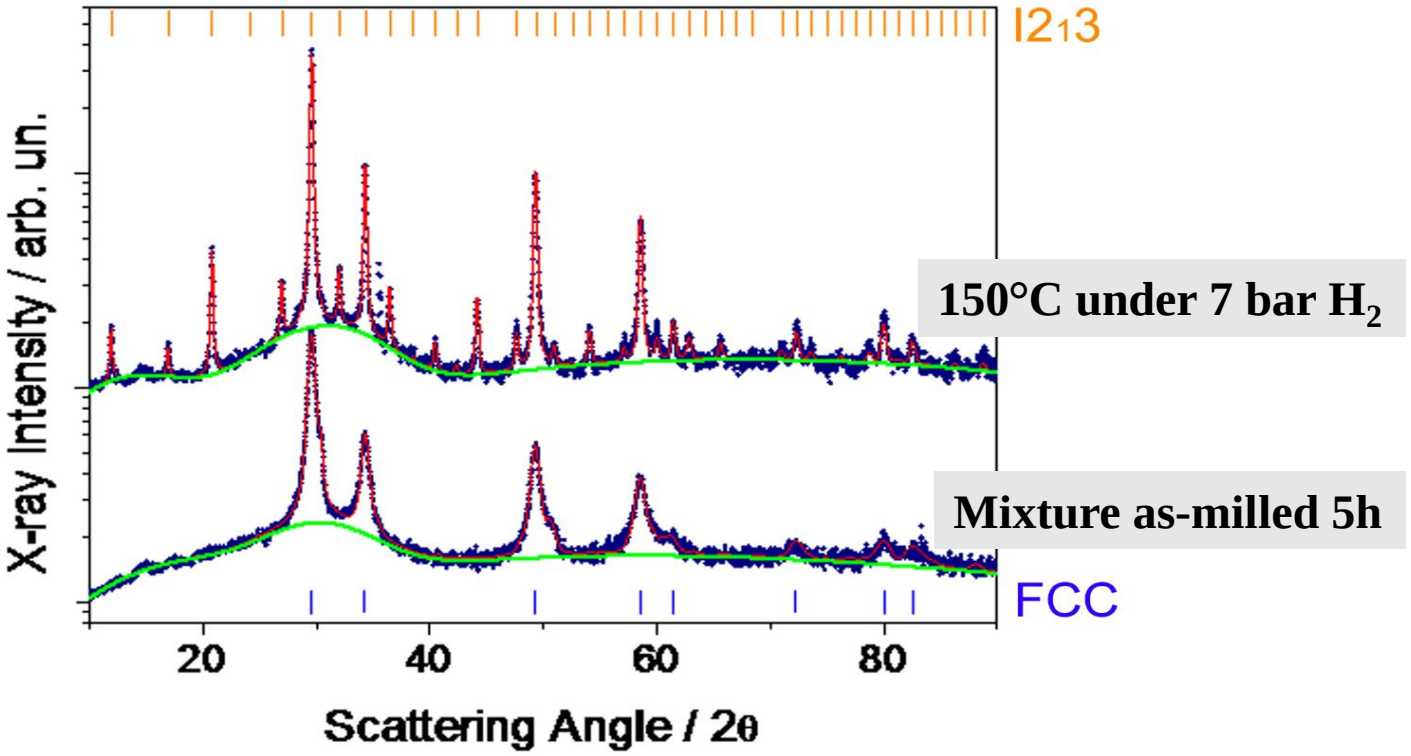

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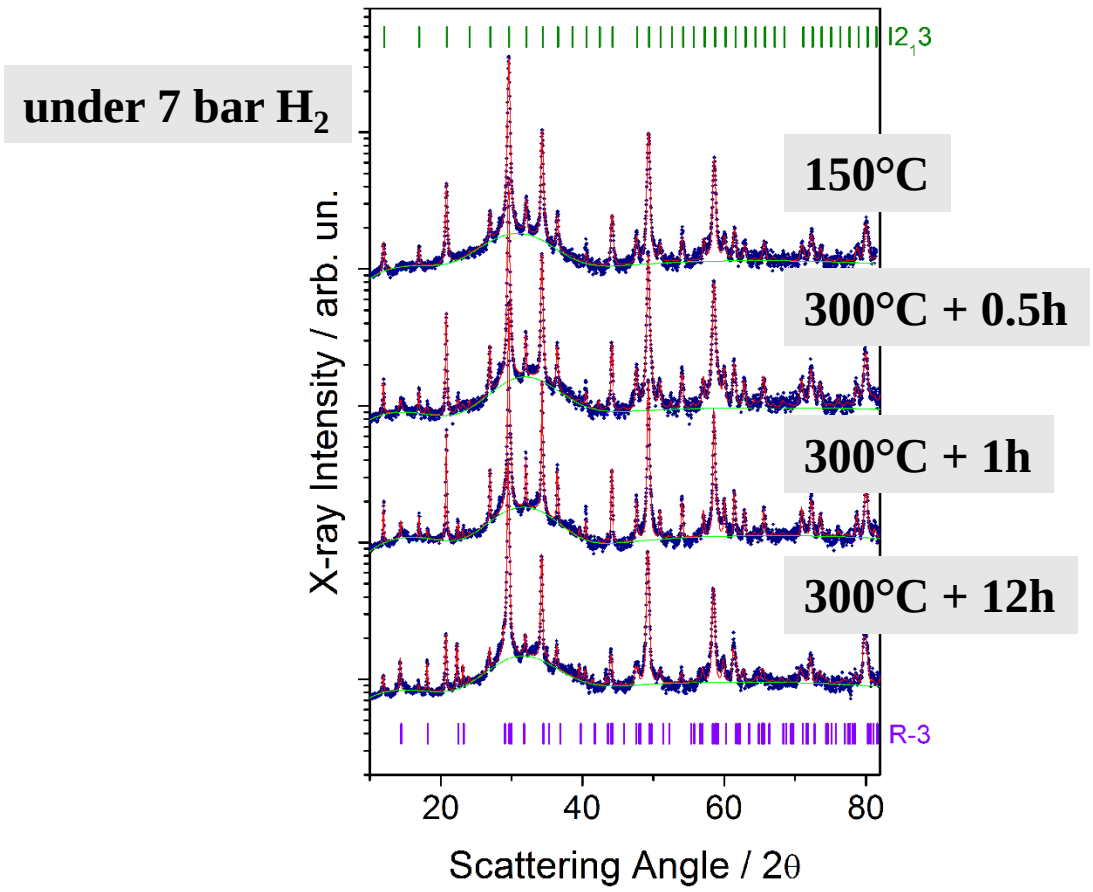

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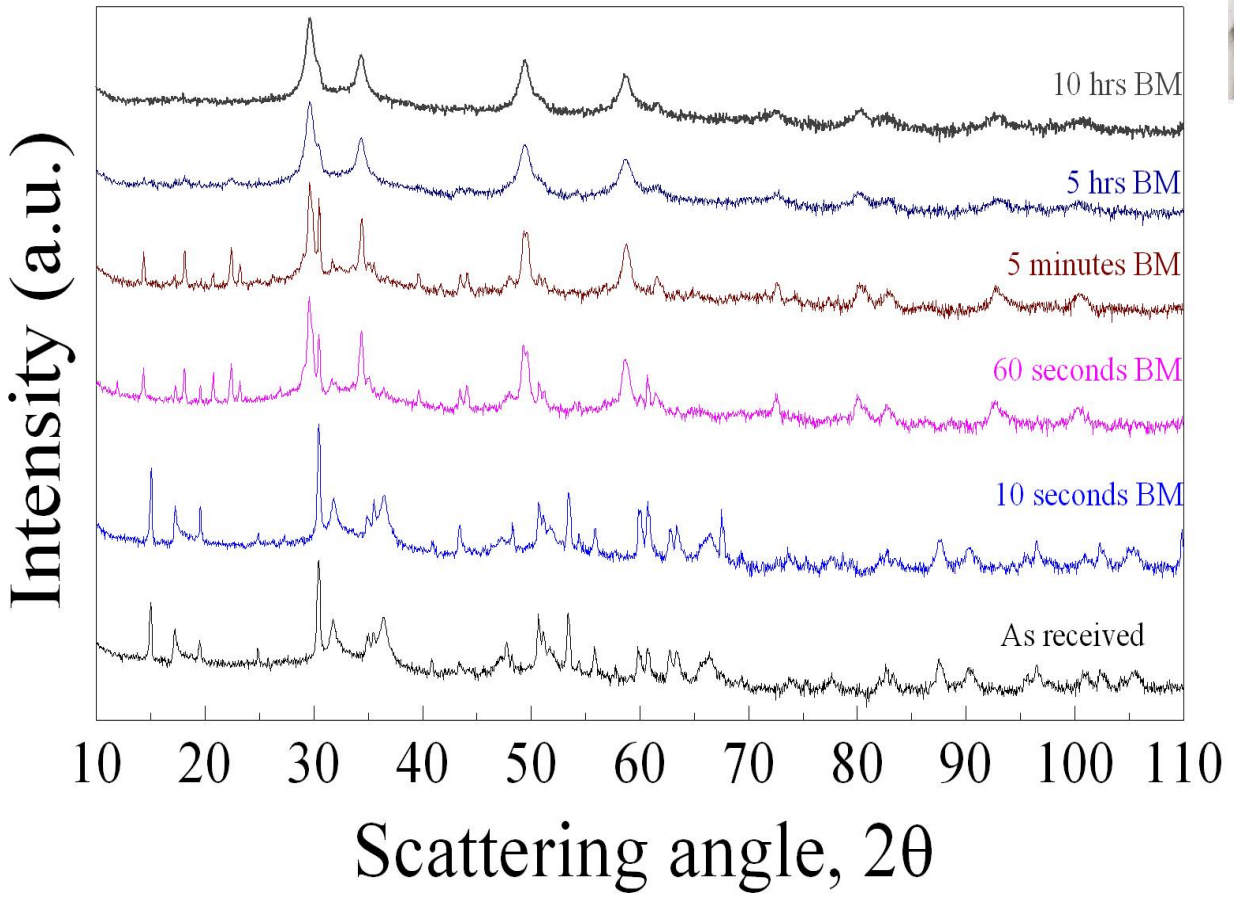
Ball to powder ratio = 1:1



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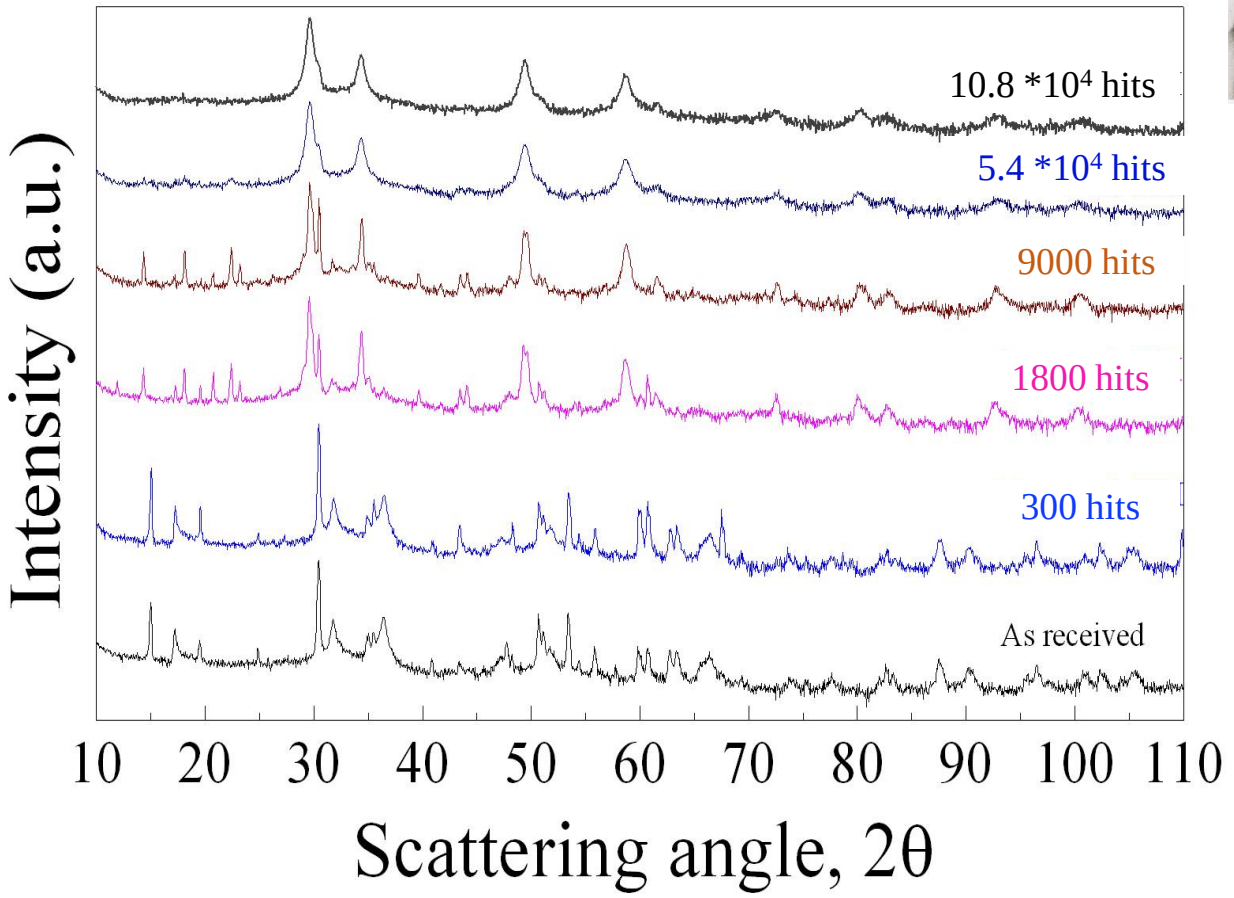

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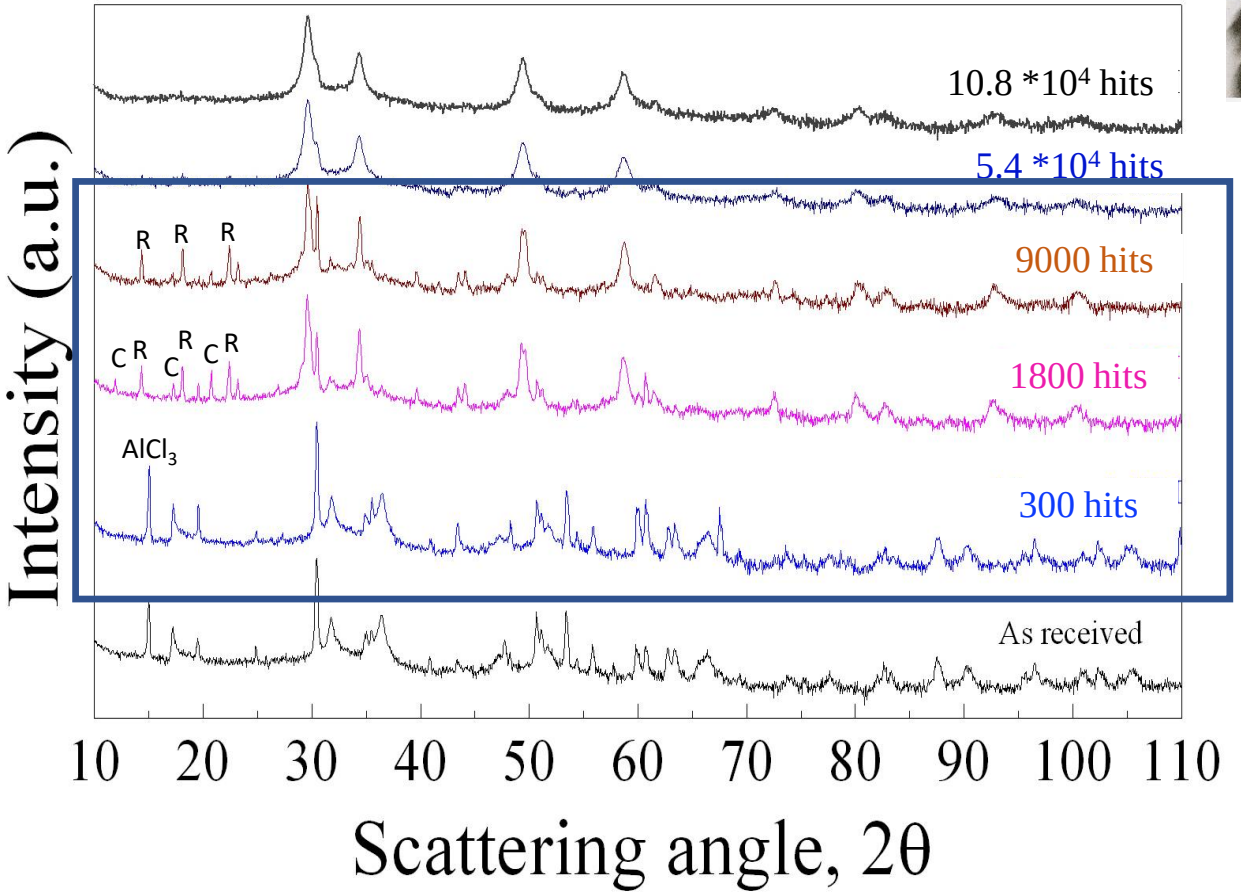

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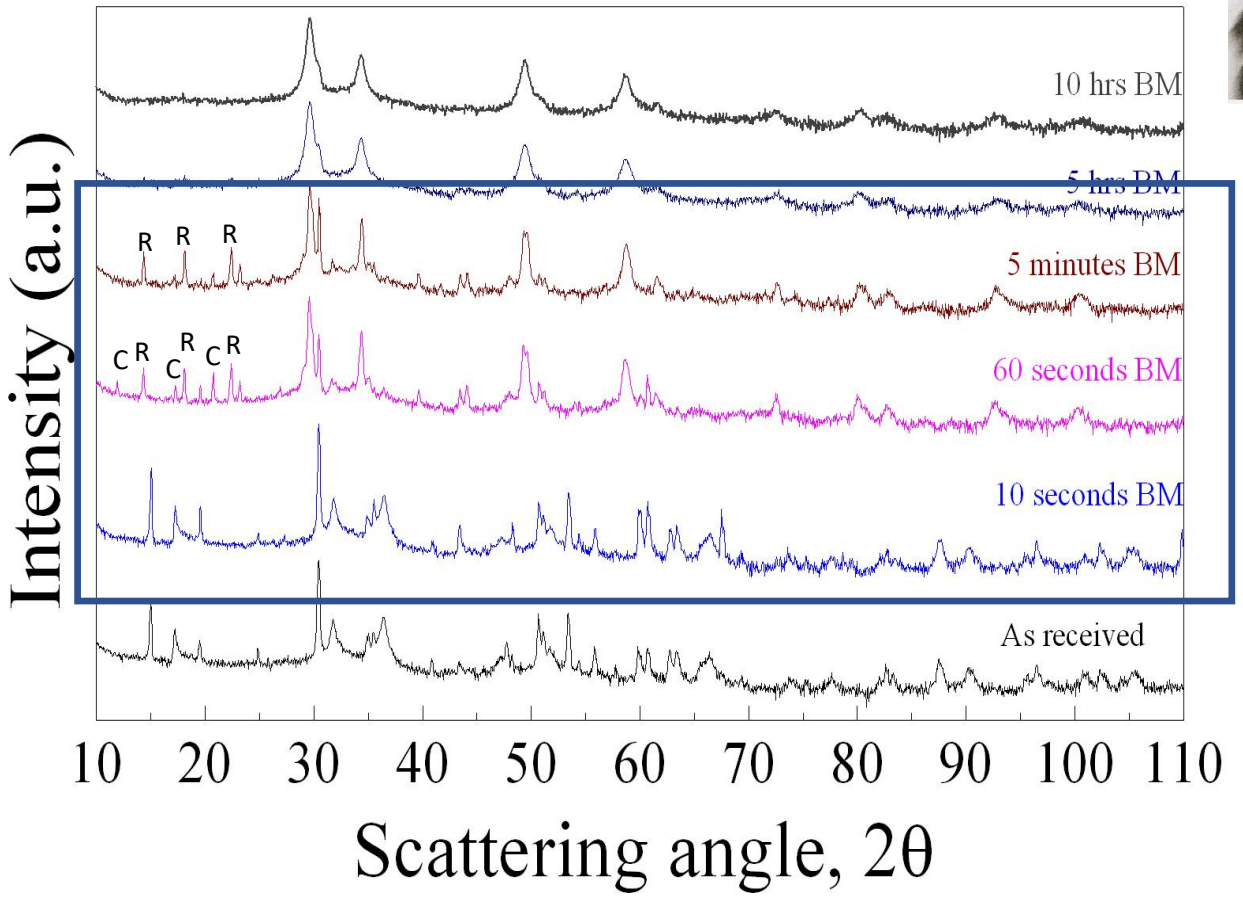

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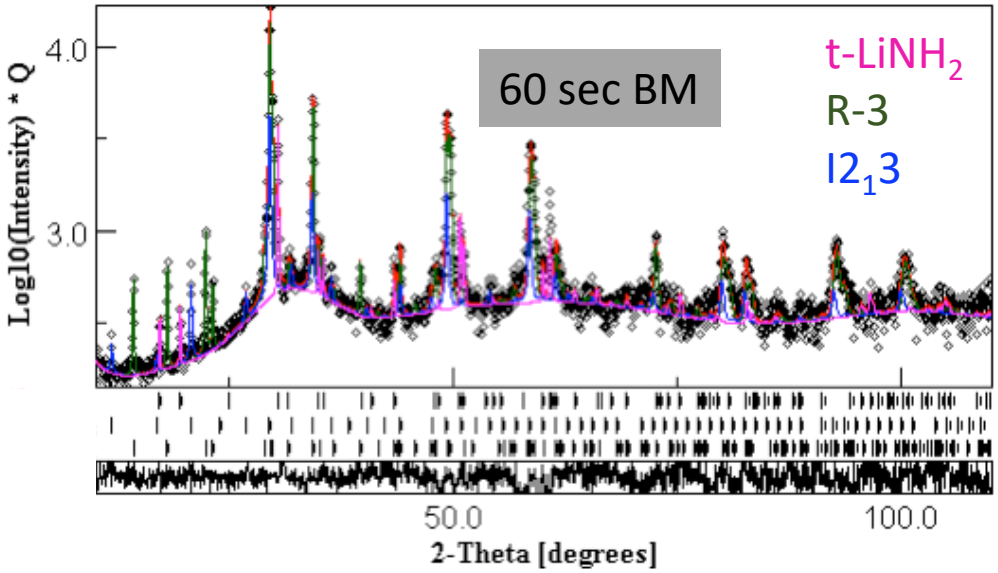

Rhombohedral R-3, *a* = 9.772 Å and *c* = 8.961 Å, 60.0 wt%

Cubic, $I2_13$, *a* = 10.458 Å, 25.0 wt%

SAME PHASES OBSERVED UPON ANNEALING OF THE SOLID SOLUTION !!!

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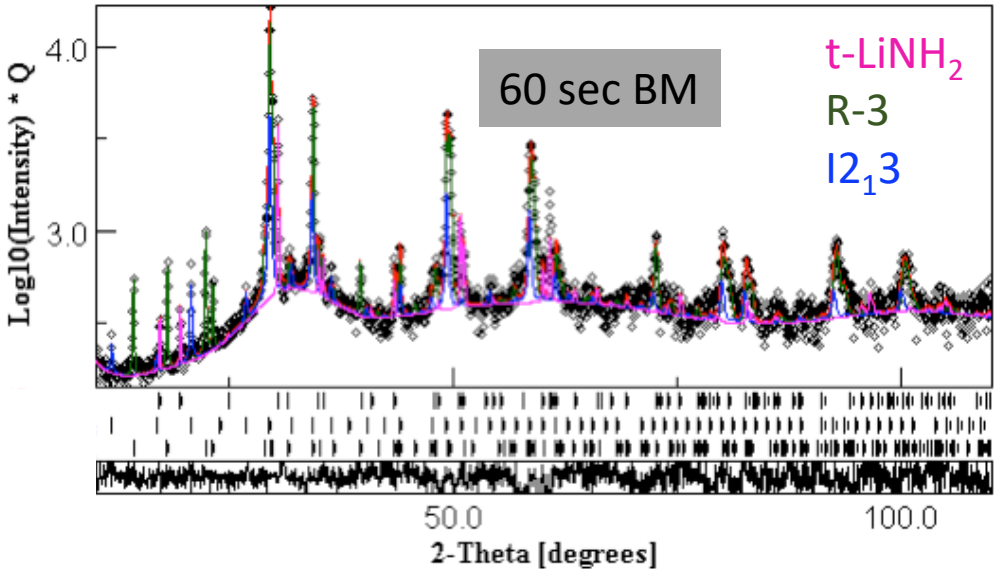

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Formation of the 2 new phases takes place in few seconds,… suggesting the occurrence of a MSR !!

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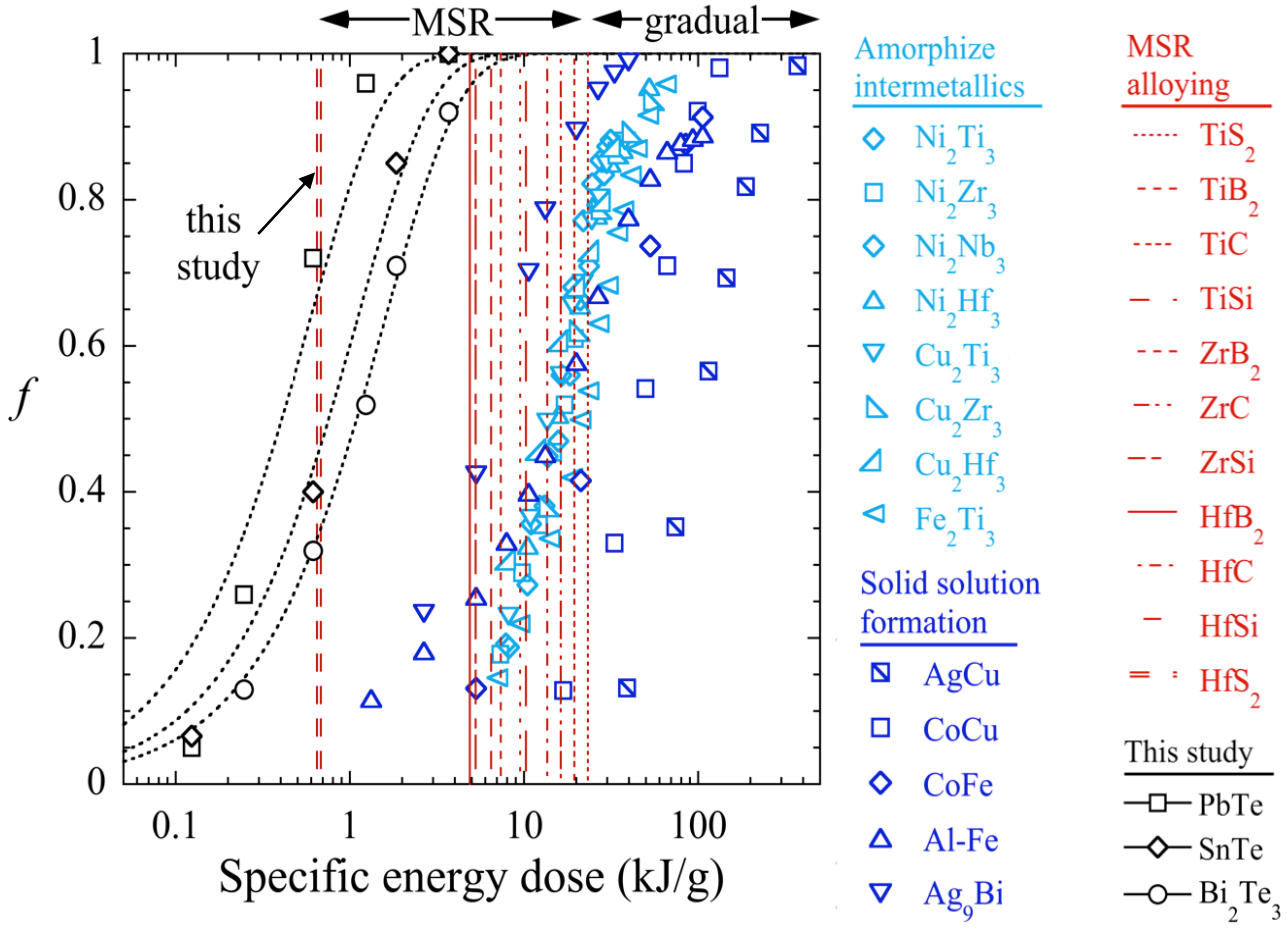
Mechanochemical reactions



[1] S.A. Humphry-Baker, S. Garroni, F. Delogu and C. Schuh, Nature Materials , 2016, DOI: 10.1038/NMAT4732

.

Mechanically induced self-propagating reaction, MSR

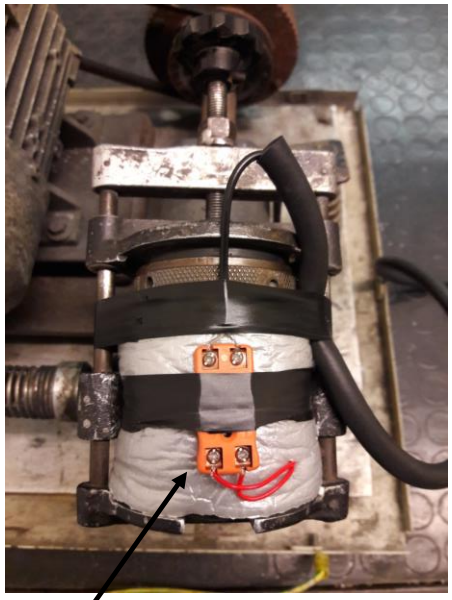
- Exothermic powder mixtures
- Activation period: size reduction, mixing, and defect formation

The MSR (mechanically induced self-propagating reaction) is ignited when the powder reaches a well defined critical state. Once started, the reaction propagates through the powder charge as a combustion process[1].

- TiC, TiS, PbTe, PbS, CdSn, ZnSn, etc…

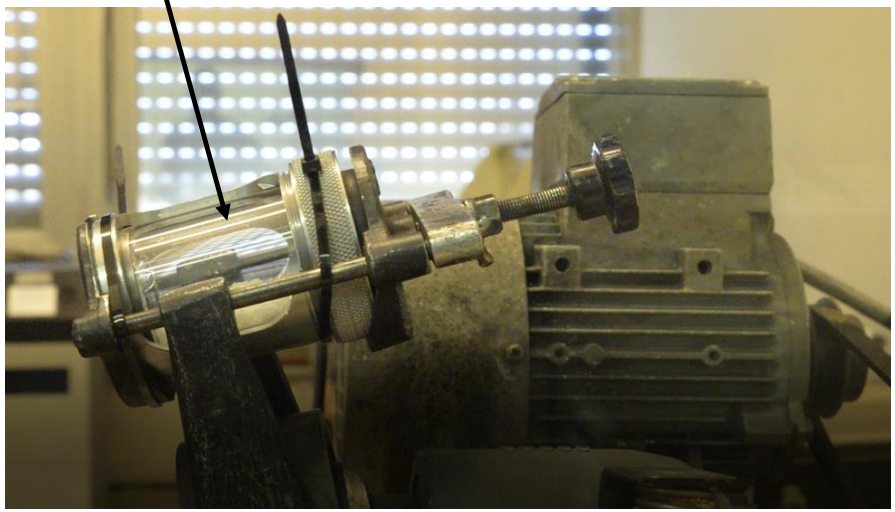
[1] Laszlo Takacs, Progress in Materials Science 47 (2002) 355–414.

MSR in the $LiNH_2$+x$AlCl_3$

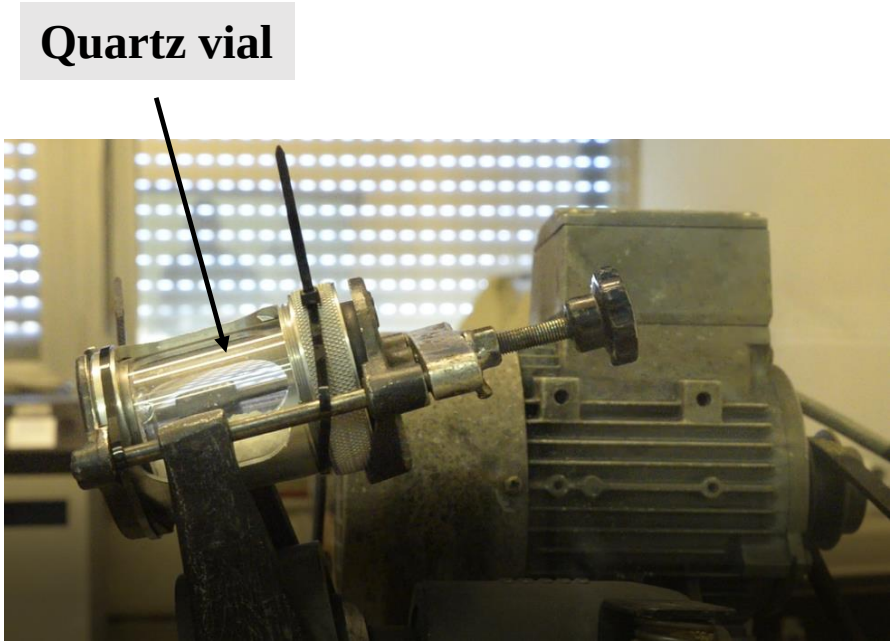


Termocouple

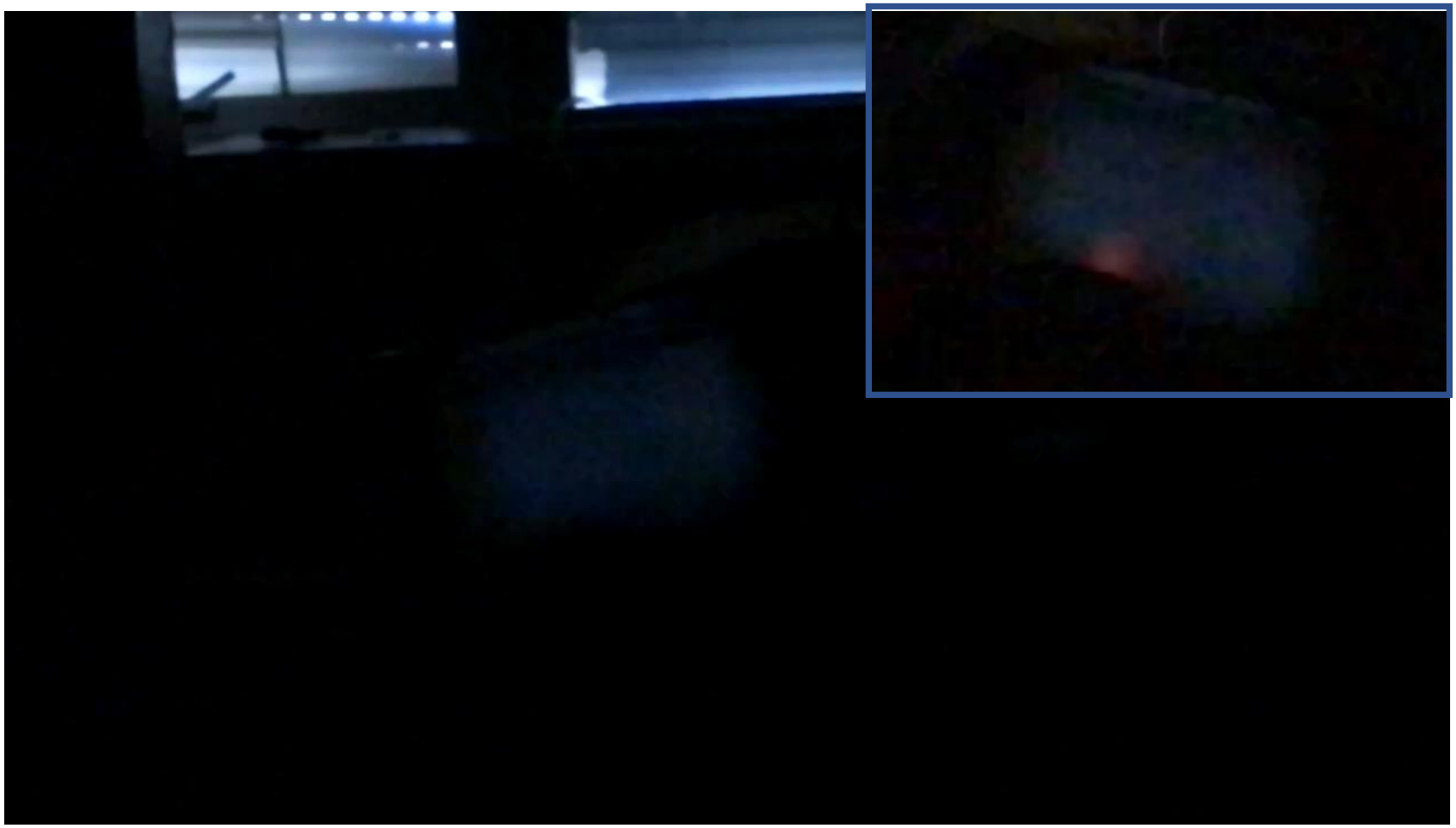
Quartz vial



MSR in the $LiNH_2$+x$AlCl_3$

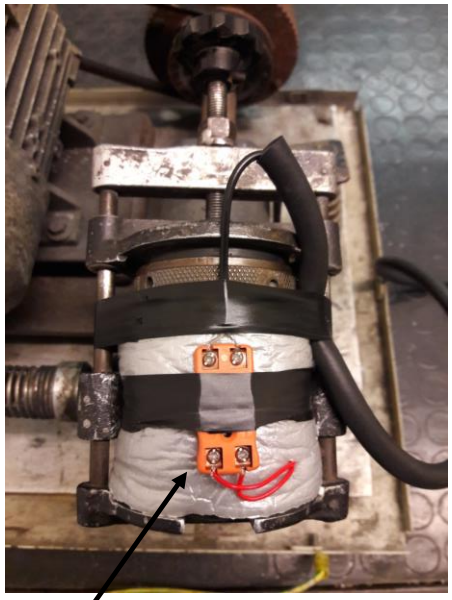


MSR in the $LiNH_2$+x$AlCl_3$

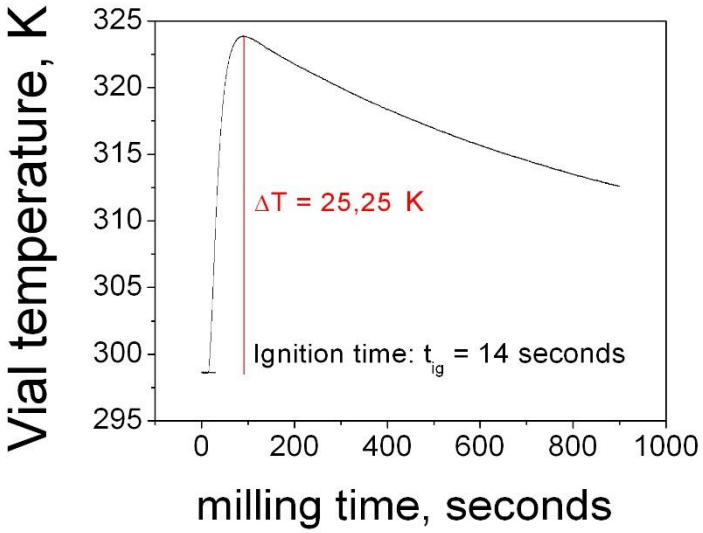


S. Garroni. **Aluminum Chloride as effective dopant in Amide-based systems**

MSR in the $LiNH_2$+x$AlCl_3$



Termocouple

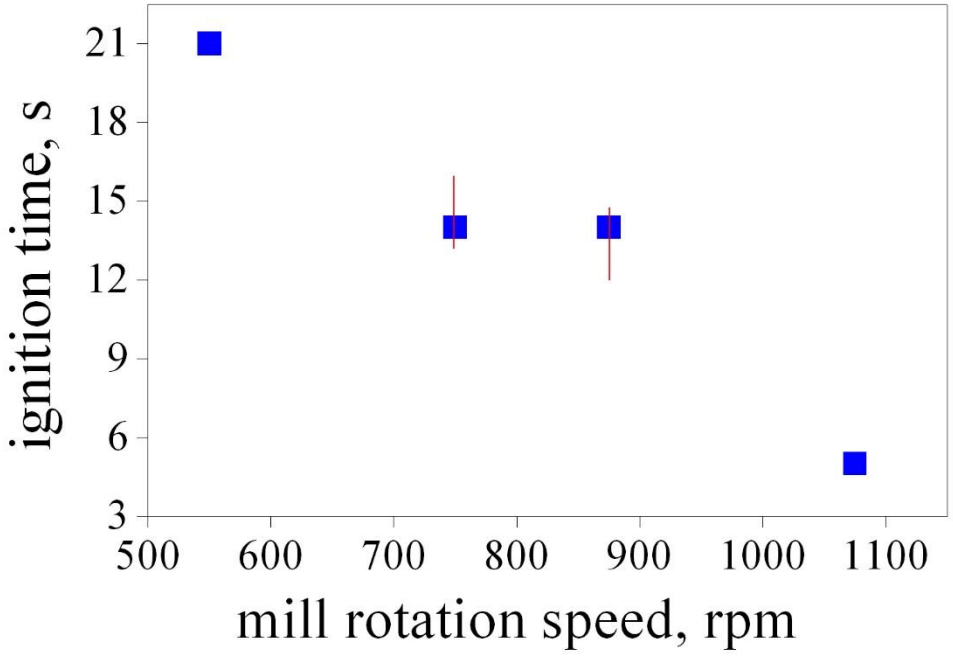


- Rotation speed
- Mass of ball
- Amount of $AlCl_3$

S. Garroni. **Aluminum Chloride as effective dopant in Amide-based systems**

MSR in the $LiNH_2$+x$AlCl_3$

MSR data vs milling rotation speed



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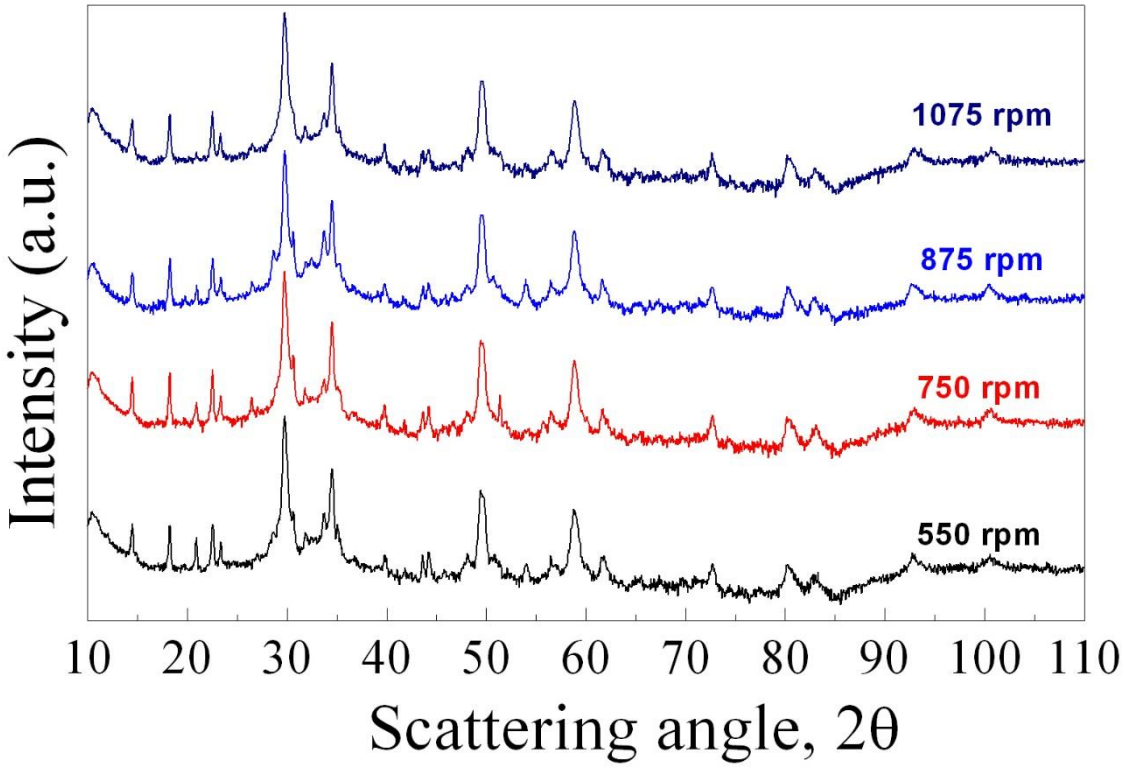
MSR in the $LiNH_2$+x$AlCl_3$

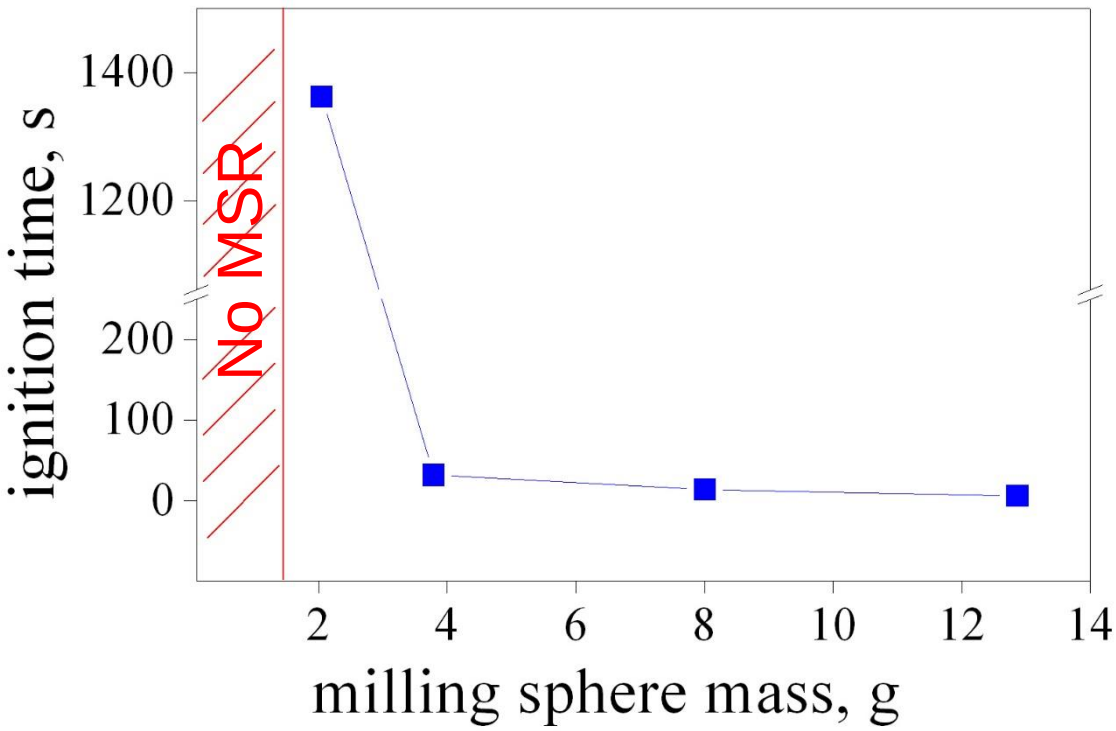
MSR data vs milling rotation speed



S. Garroni. **Aluminum Chloride as effective dopant in Amide-based systems**

MSR in the $LiNH_2$+x$AlCl_3$

MSR data vs milling sphere mass



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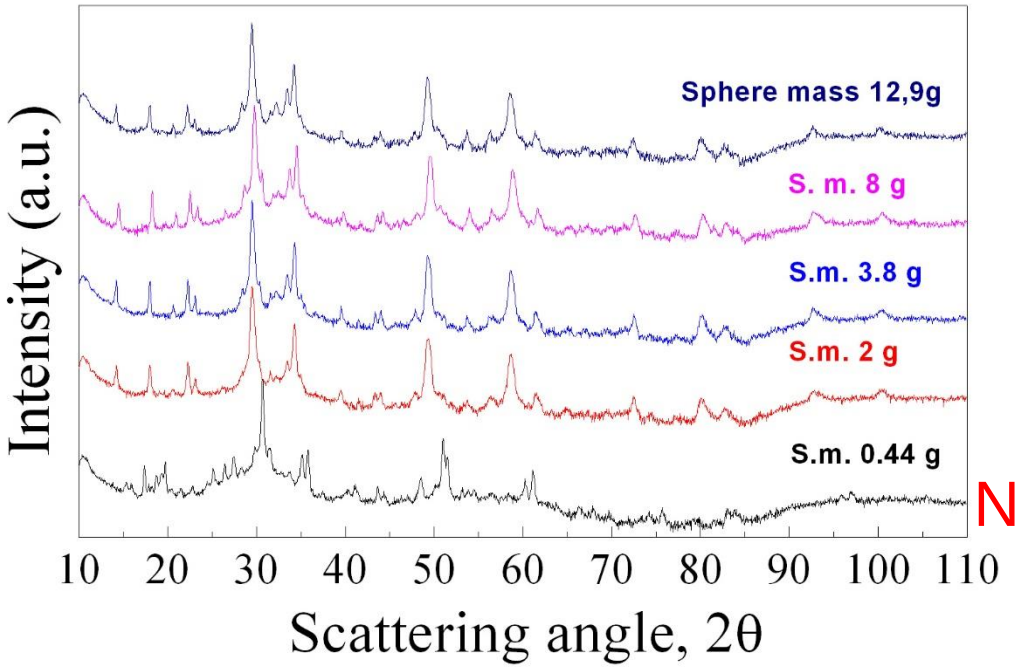
MSR in the $LiNH_2$+x$AlCl_3$

MSR data vs milling sphere mass

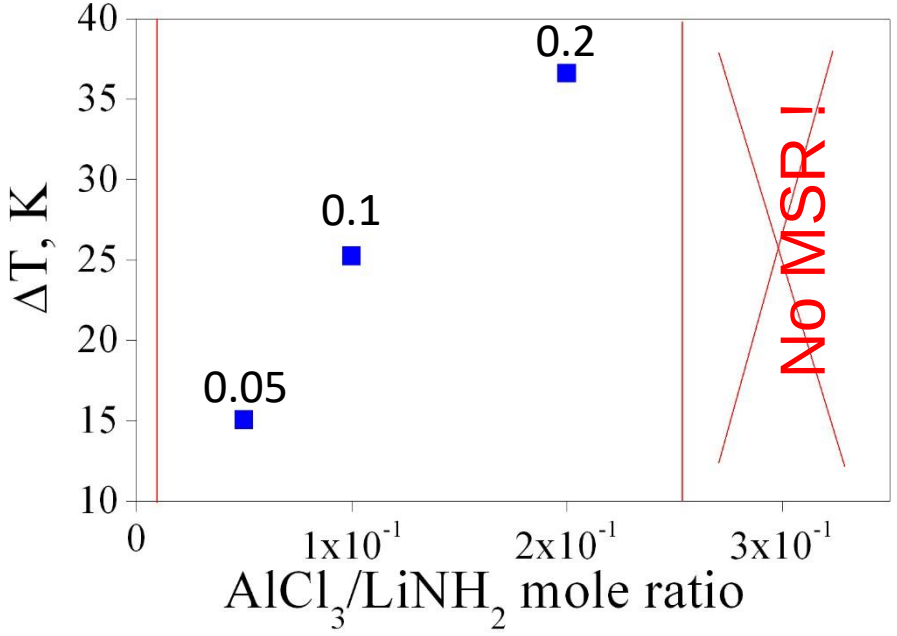


No MSR !

S. Garroni. **Aluminum Chloride as effective dopant in Amide-based systems**

MSR in the $LiNH_2$+x$AlCl_3$

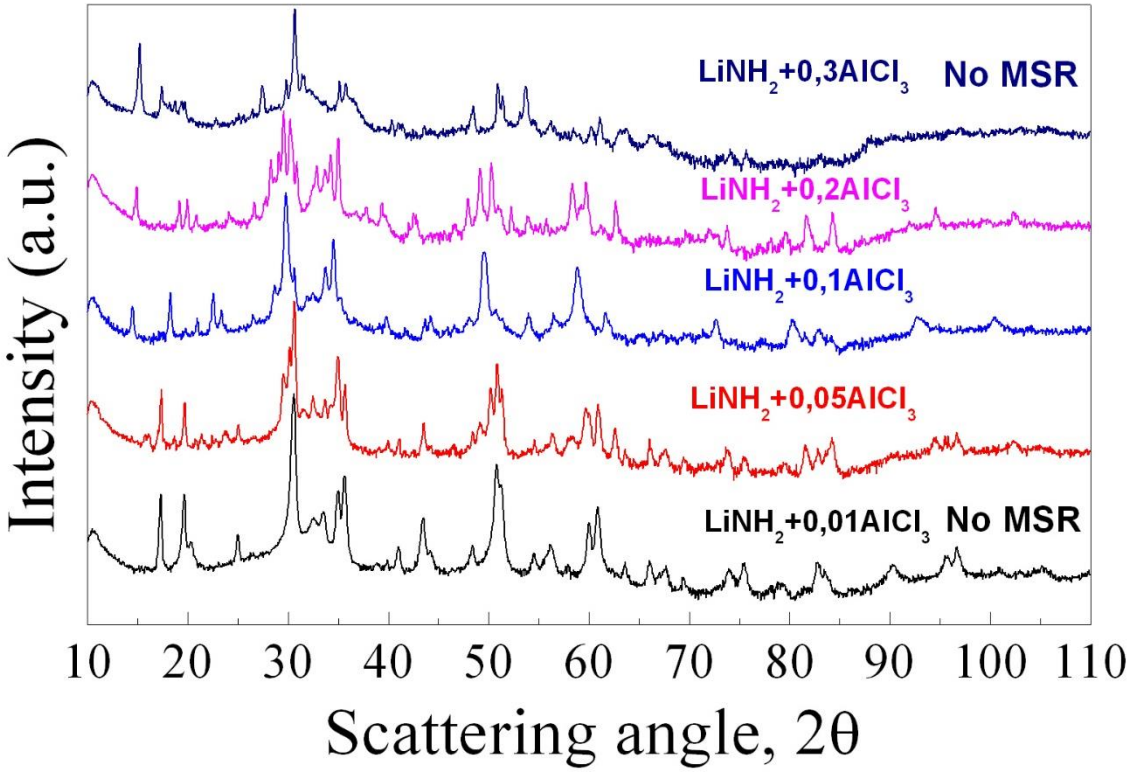
MSR data vs $AlCl_3$ content



S. Garroni. **Aluminum Chloride as effective dopant in Amide-based systems**

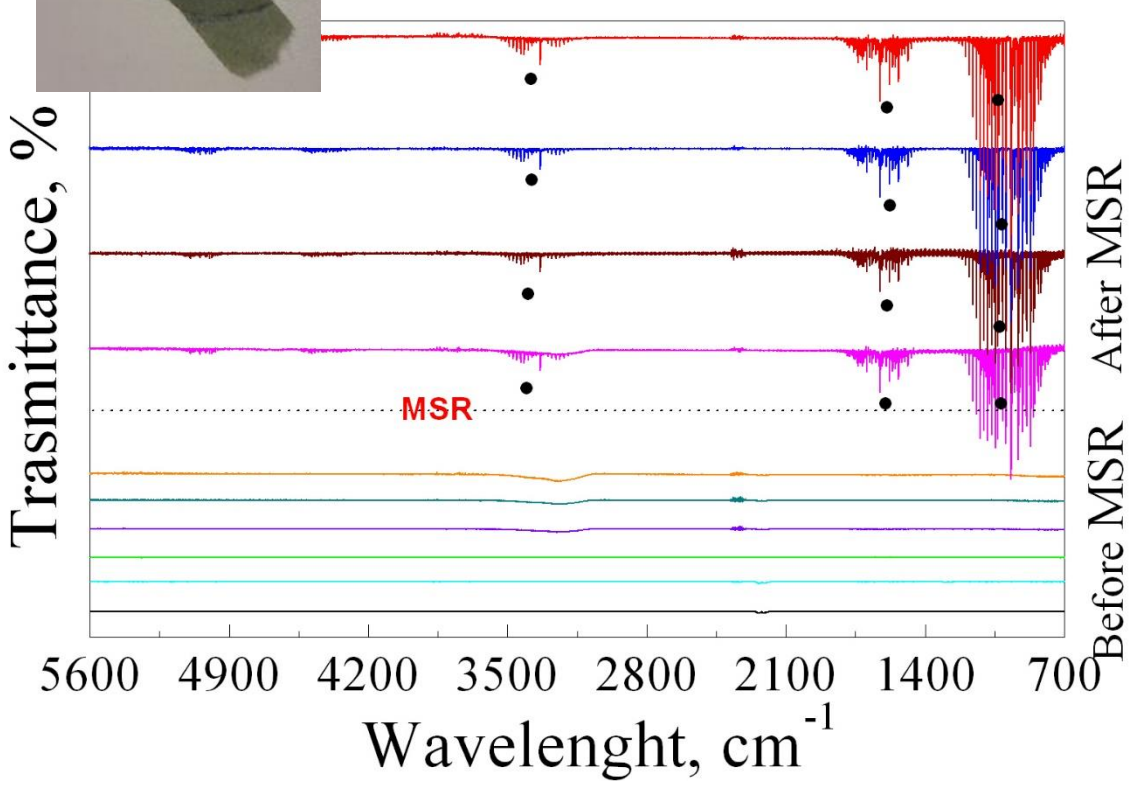
MSR in the $LiNH_2$+x$AlCl_3$

MSR data vs $AlCl_3$ content

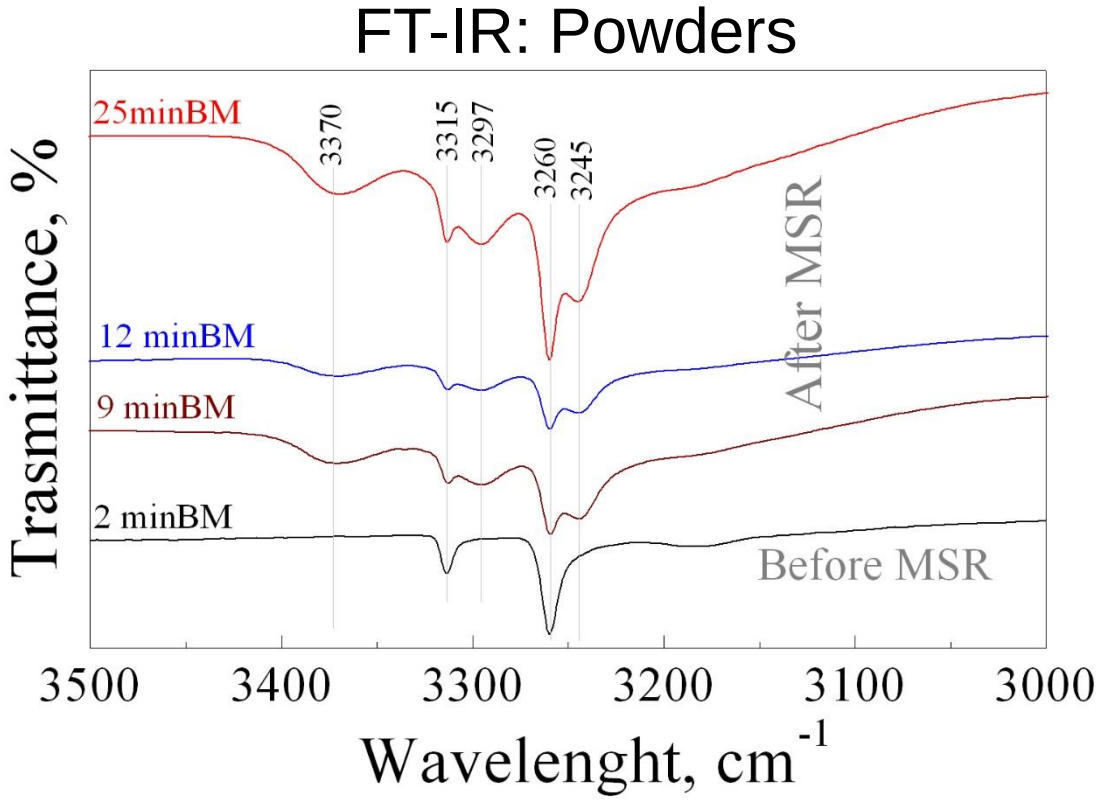


S. Garroni. **Aluminum Chloride as effective dopant in Amide-based systems**

MSR in the $LiNH_2$+x$AlCl_3$



MSR in the $LiNH_2$+x$AlCl_3$



Conclusions

- $AlCl_3$ represents a good additive to improve the hydrogen sorption properties of the MNH_2 – based systems
- Among the halide-baed additives, $AlCl_3$ is one of the most performing
- The active phase is mainly composed by Li-Al-N-H-Cl
- Two new hydrogen phases have been discovered
- These phases can be obtained after a thermal annealing of the solid solution FCC produced by ball milling (5h) or……
- In few seconds by MSR
- For the first time a MSR took place in complex hydride based systems

Conclusions

- Both the crystal structures of the new hydride phases are not solved
- No MSR reaction occurred with LiH. Why?
- Thermodanymic data about the new phases are still missing

- New opportunities in the synthesis of amide-based phases as hydrogen storage materials
- $NaNH_2 + xAlCl_3$?, $Mg(NH_2)_2 + xAlCl_3$?....

Acknowledgments

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PhD stduent Nina Senes
Lucia Pisano

Prof. Fabiana Gennari
Dr. Luisa Fernandez
Dr. Nadia Gamba
Dr. Guillermina Amica

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Lucia Pisano

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Universitat Autònoma de Barcelona

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Dr. Luisa Fernandez
Dr. Nadia Gamba
Dr. Guillermina Amica

EUROPEAN COMMISSION

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Helmholtz-Zentrum Geesthacht
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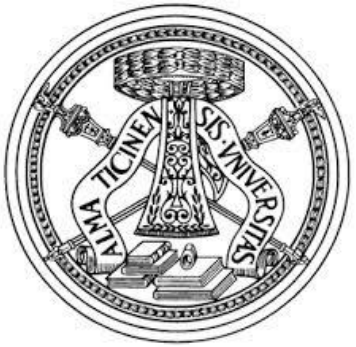
Prof. Martin Dornheim



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Dr. Alessandro Girella

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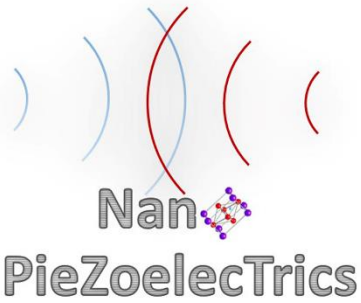
ICCRAM
INTERNATIONAL RESEARCH CENTER IN CRITICAL RAW MATERIALS FOR ADVANCED INDUSTRIAL TECHNOLOGIES



Acknowledgments

Thank you for your attention

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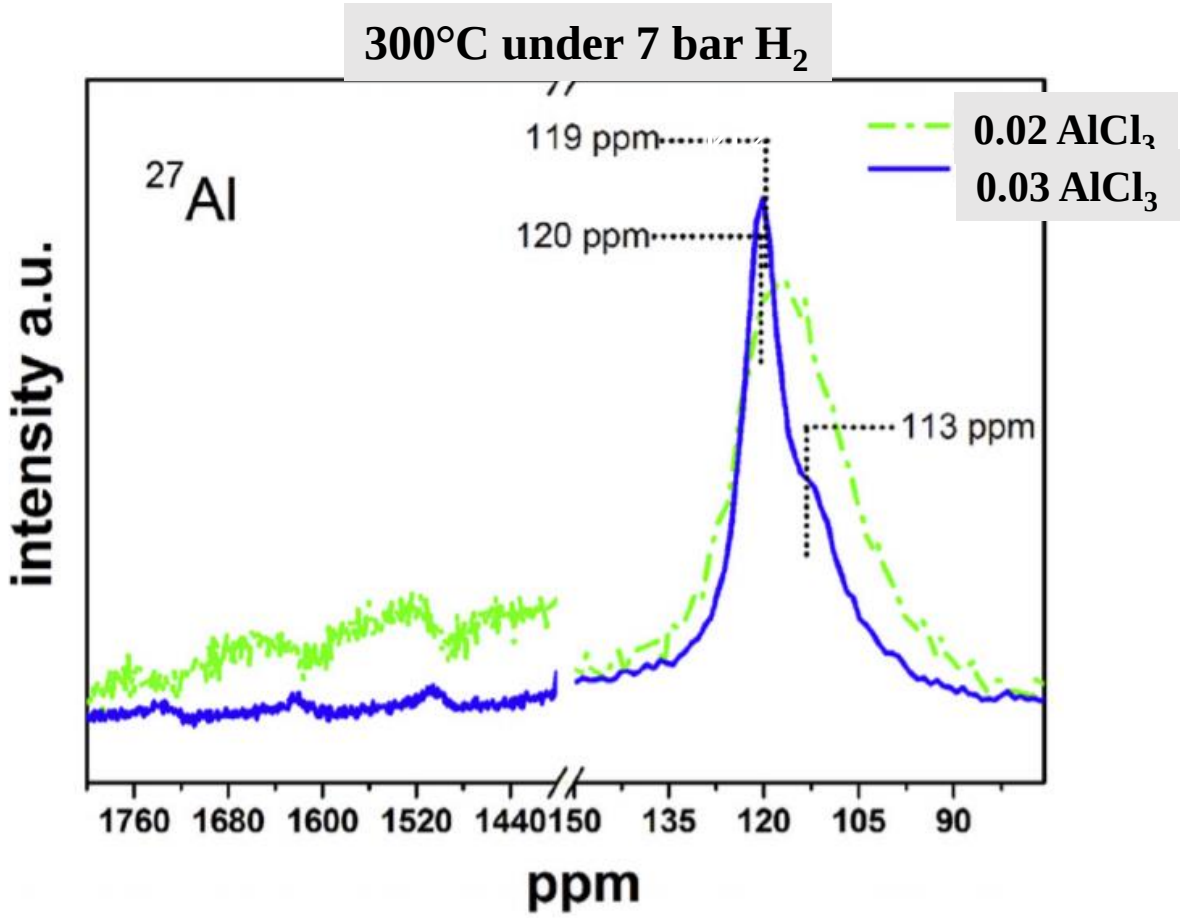
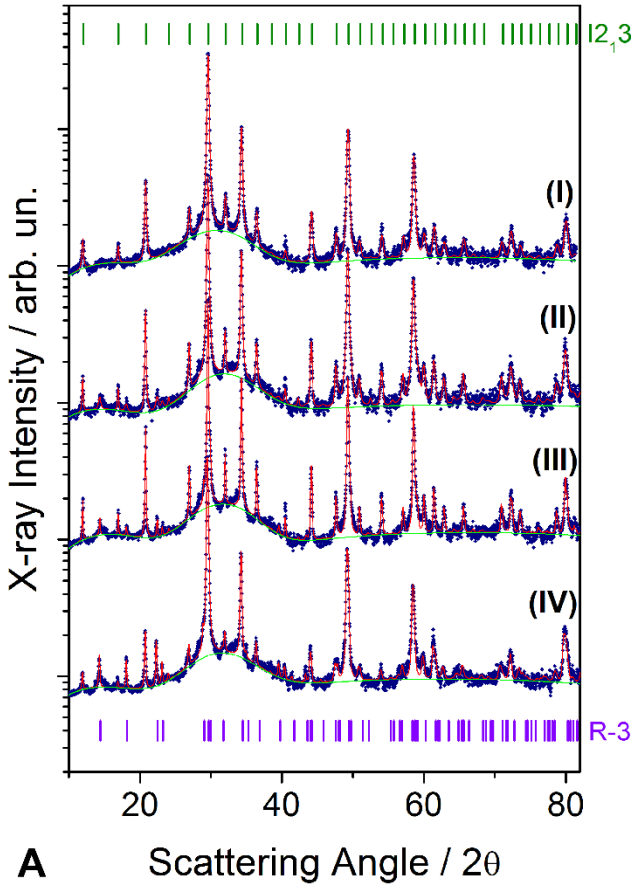
Structural Investigation: Upon annealing – MAS NMR



[1] Fernandez Albanesi L, Garroni S., Arneodo Lorochette P, Nolis, P., Mulas G., Enzo S., Barò M.D., Gennari FC. Int J Hydrogen Energy 2015;40,:13506-17.

Materials for hydrogen storage



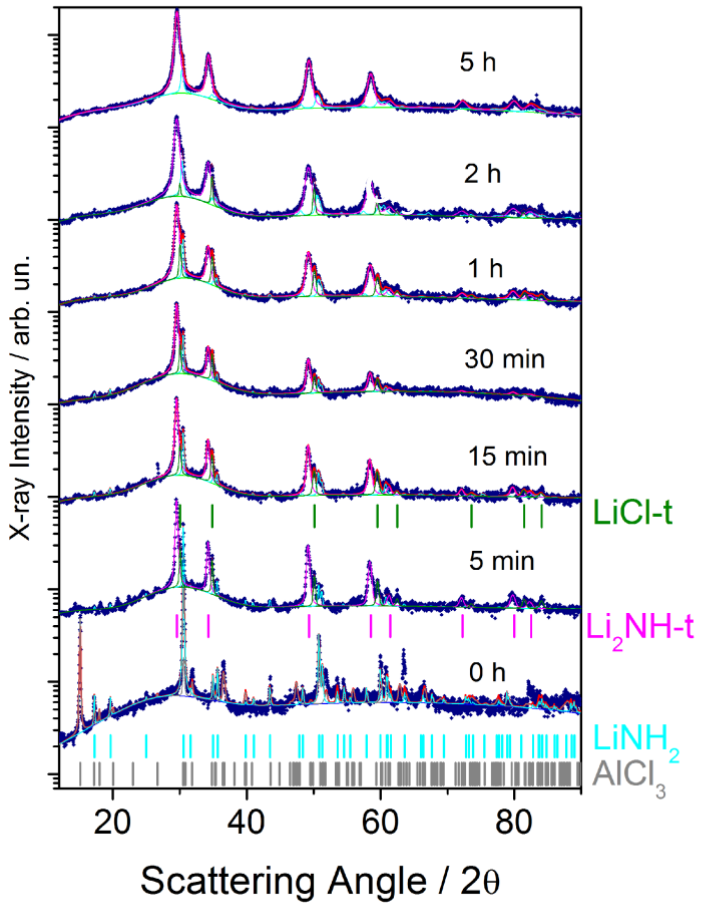
S. Garroni. **Aluminum Chloride as effective dopant in Amide-based systems**

Improving hydrogen storage properties: catalysts

[1] Chen P, et al., Interaction of hydrogen with metal nitrides and imides. Nature 2002;420-421:302-4.
[2] Chen P. et al., Nature Reviews Materials 1, 16059 (2016)

$LiNH_2 + 0.03AlCl_3$

Ball to powder ratio = 20:1



[1] Fernandez Albanesi L, Garroni S., G., Enzo S., Gennari FC. : Dalton Trans., 2016, 45, 5808.

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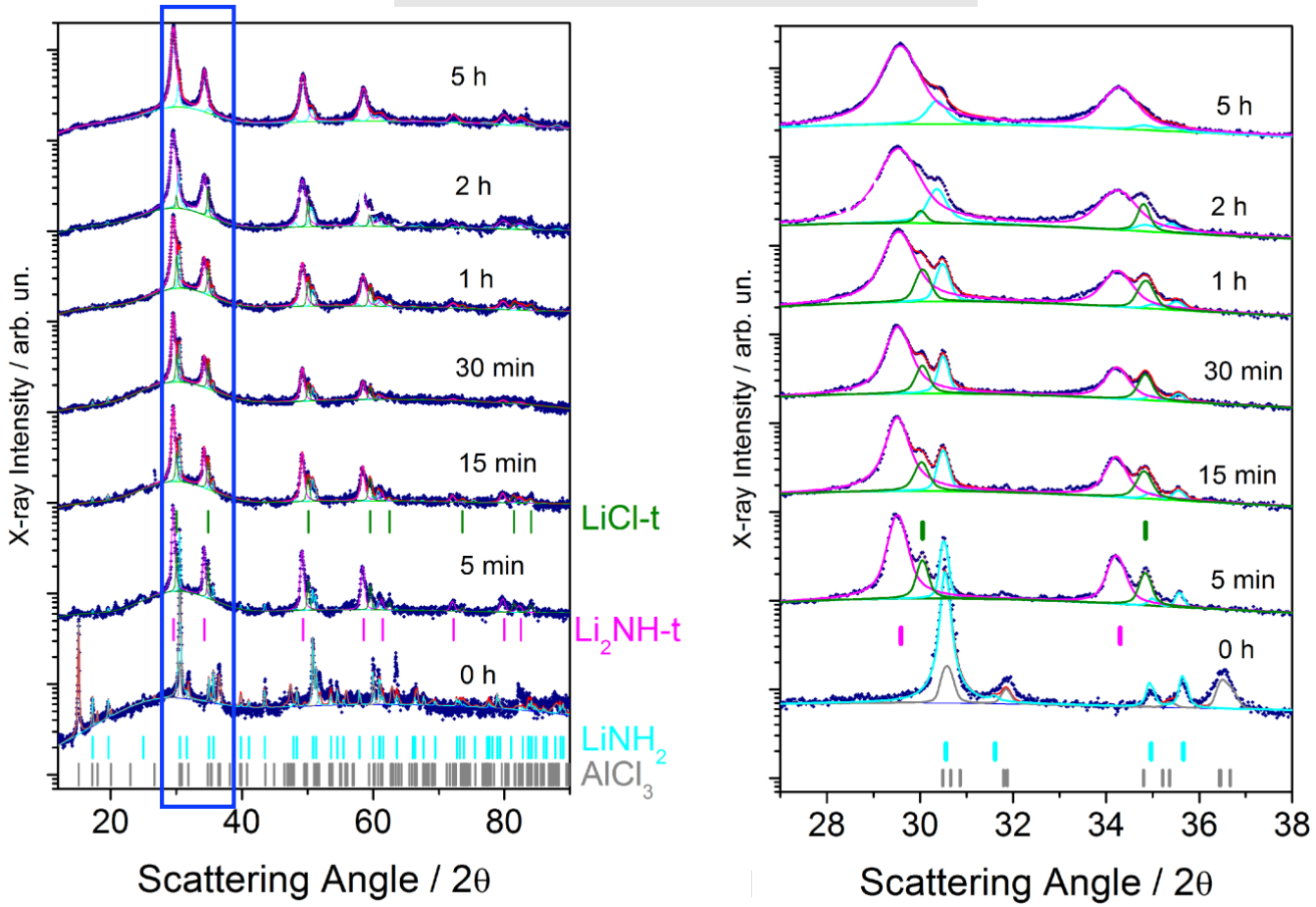
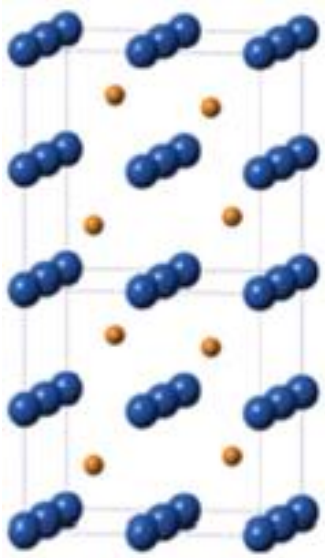


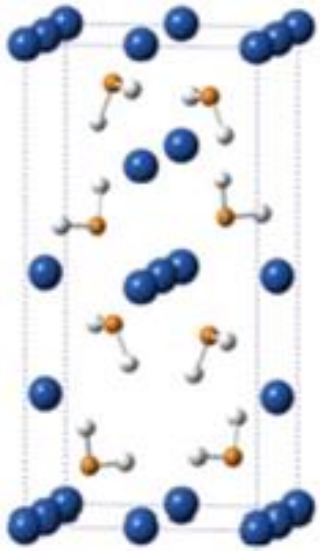
[1] Fernandez Albanesi L, Garroni S., G., Enzo S., Gennari FC. : Dalton Trans., 2016, 45, 5808.

Incorporation of AlCl3

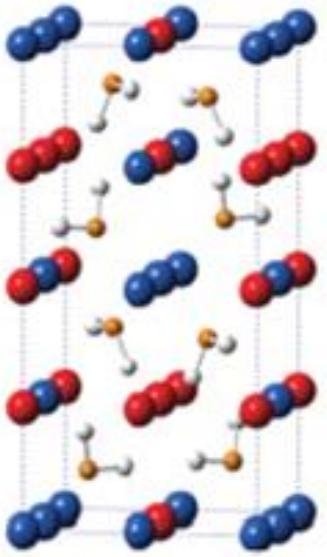


- Li_2NH

(with the origin shifted by ¼, ¼, ¼)



- $LiNH_2$



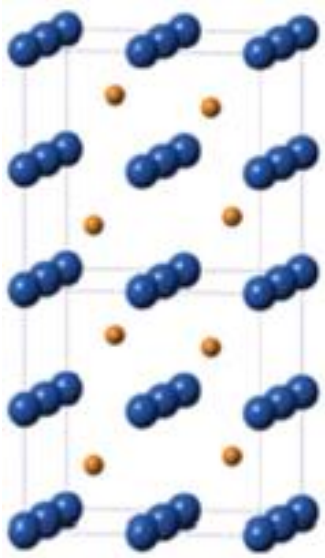
- $LiNH_2$

(with vacant lithium side showed in red)

- The ball milling of $LiNH_2$ with $AlCl_3$ easy creates $Li_{1+x}NH_{2-x}$ amide-imide solid solutions

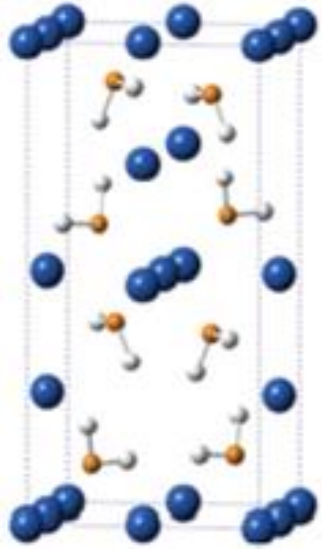
[1] David WIF, Jones MO, Gregory DH, Jewell CM, Johnson SR, Walton A, et al. A mechanism for non-stoichiometry in the lithium amide/lithium imide hydrogen storage reaction. J Am Chem Soc 2007;129:1594e601.

Incorporation of AlCl3

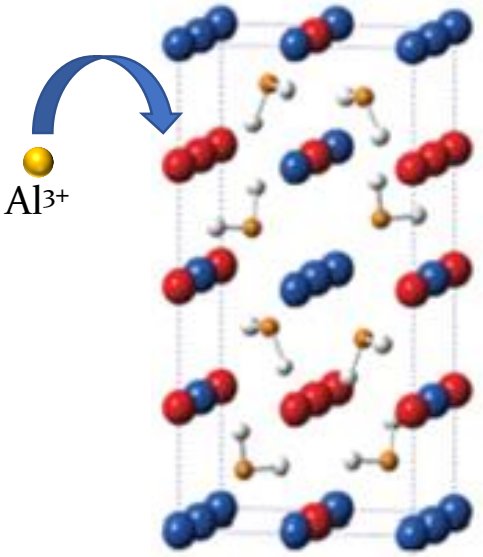


- Li_2NH

(with the origin shifted by ¼, ¼, ¼)



- $LiNH_2$



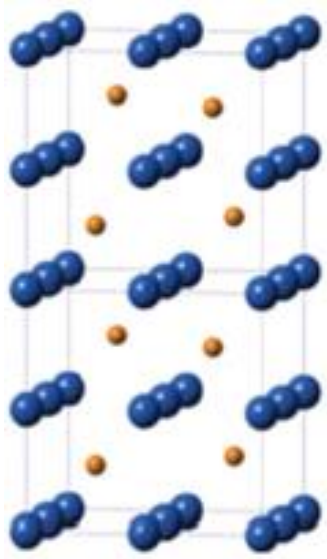
- $LiNH_2$

(with vacant lithium side showed in red)

- The Al^{3+} ions could replace sites normally reserved for Li^+ (in the cubic description, 50% are empty).

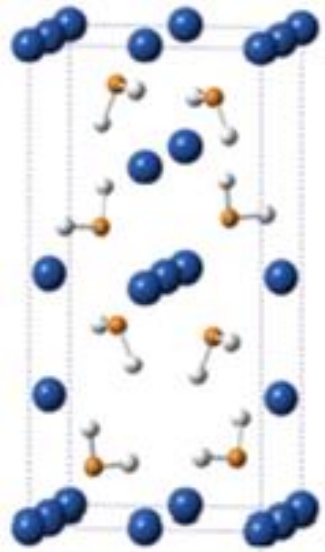
[1] David WIF, Jones MO, Gregory DH, Jewell CM, Johnson SR, Walton A, et al. A mechanism for non-stoichiometry in the lithium amide/lithium imide hydrogen storage reaction. J Am Chem Soc 2007;129:1594e601.

Incorporation of AlCl3

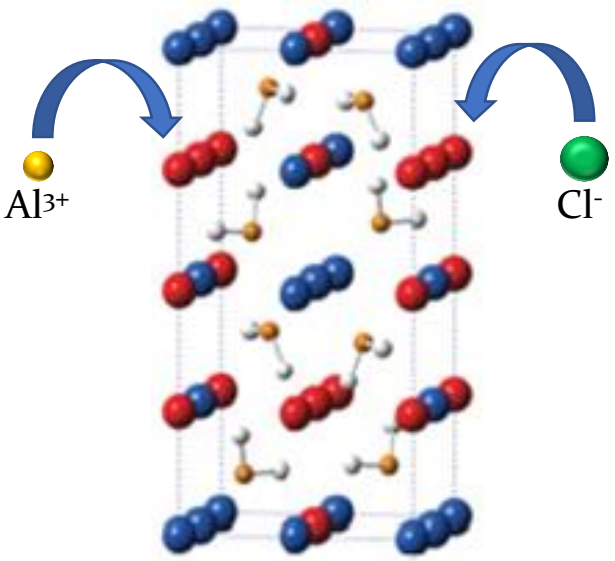


- Li_2NH

(with the origin shifted by ¼, ¼, ¼)



- $LiNH_2$



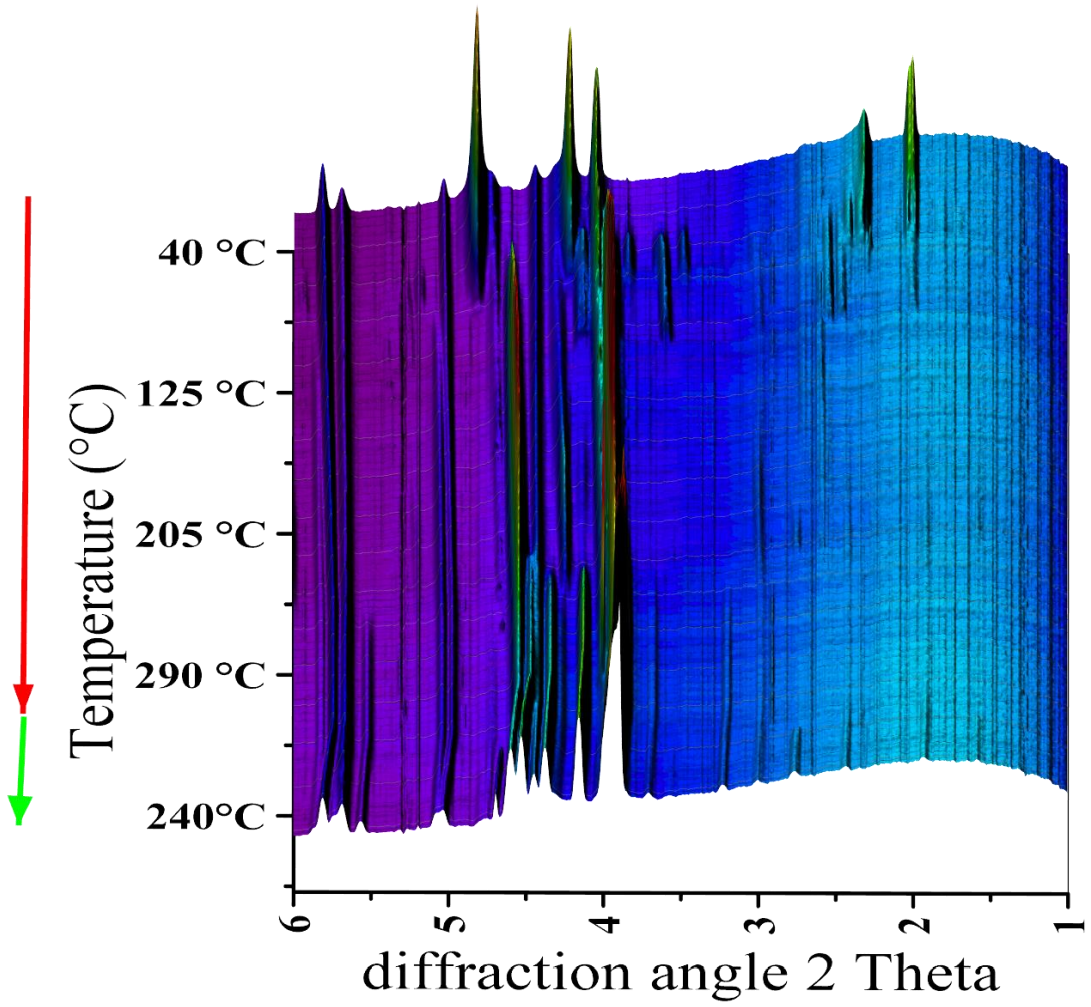
- $LiNH_2$

(with vacant lithium side showed in red)

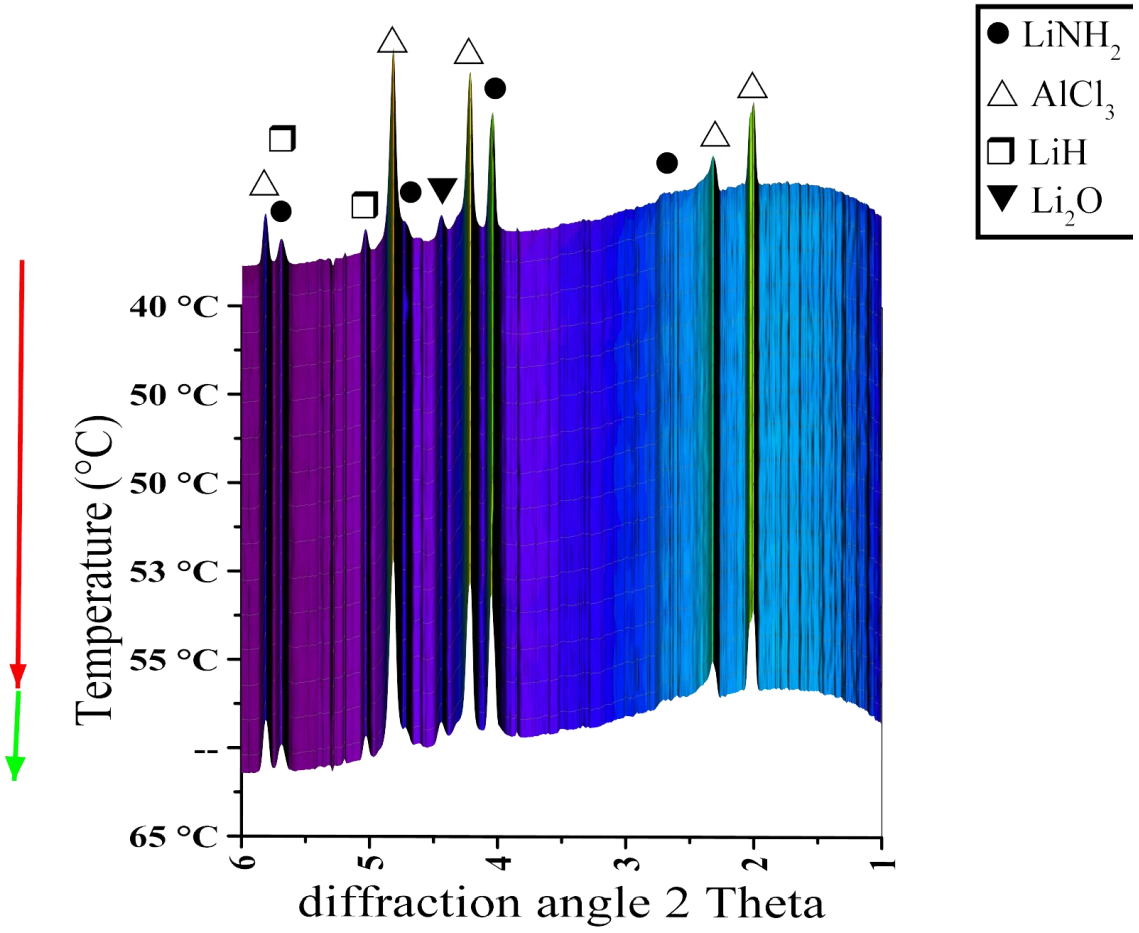
- To keep electro neutrality, the Cl ions could occupy the other empty sites

[1] *David WIF, Jones MO, Gregory DH, Jewell CM, Johnson SR, Walton A, et al. A mechanism for non-stoichiometry in the lithium amide/lithium imide hydrogen storage reaction. J Am Chem Soc 2007;129:1594e601.*

SR-XPRD

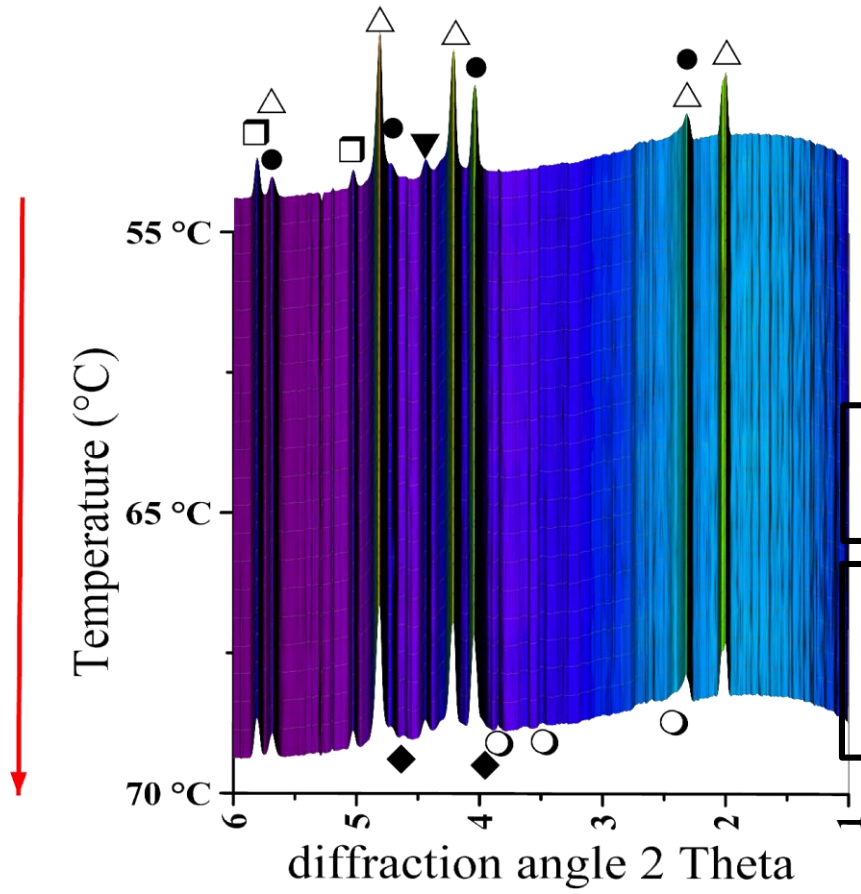

40 °C
125 °C
205 °C
290 °C
240°C
Temperature (°C)
6
5
4
3
2
1
diffraction angle 2 Theta

SR-XPRD



S. Garroni. **Aluminum Chloride as effective dopant in Amide-based systems**

SR-XPRD



$AlCl_3$:NH_3

$2LiNH_2 + AlCl_3 \rightarrow AlCl_3{:}NH_3 + Li_2NH$

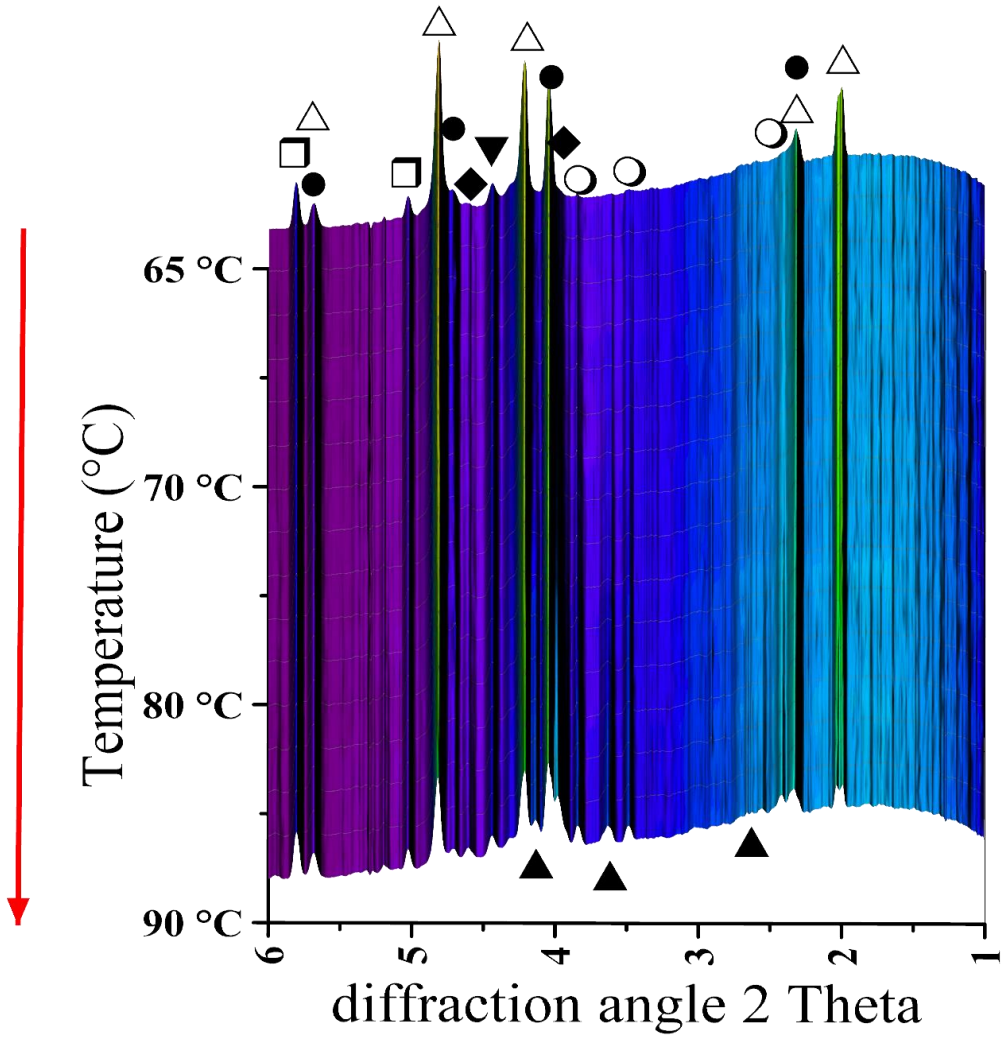
LiCl

$LiNH_2 + AlCl_3 \rightarrow LiCl + Al + H_2/NH_3$ (????)

$LiH + AlCl_3 \rightarrow LiCl + Al + H_2$ (????)

S. Garroni. **Aluminum Chloride as effective dopant in Amide-based systems**

SR-XPRD

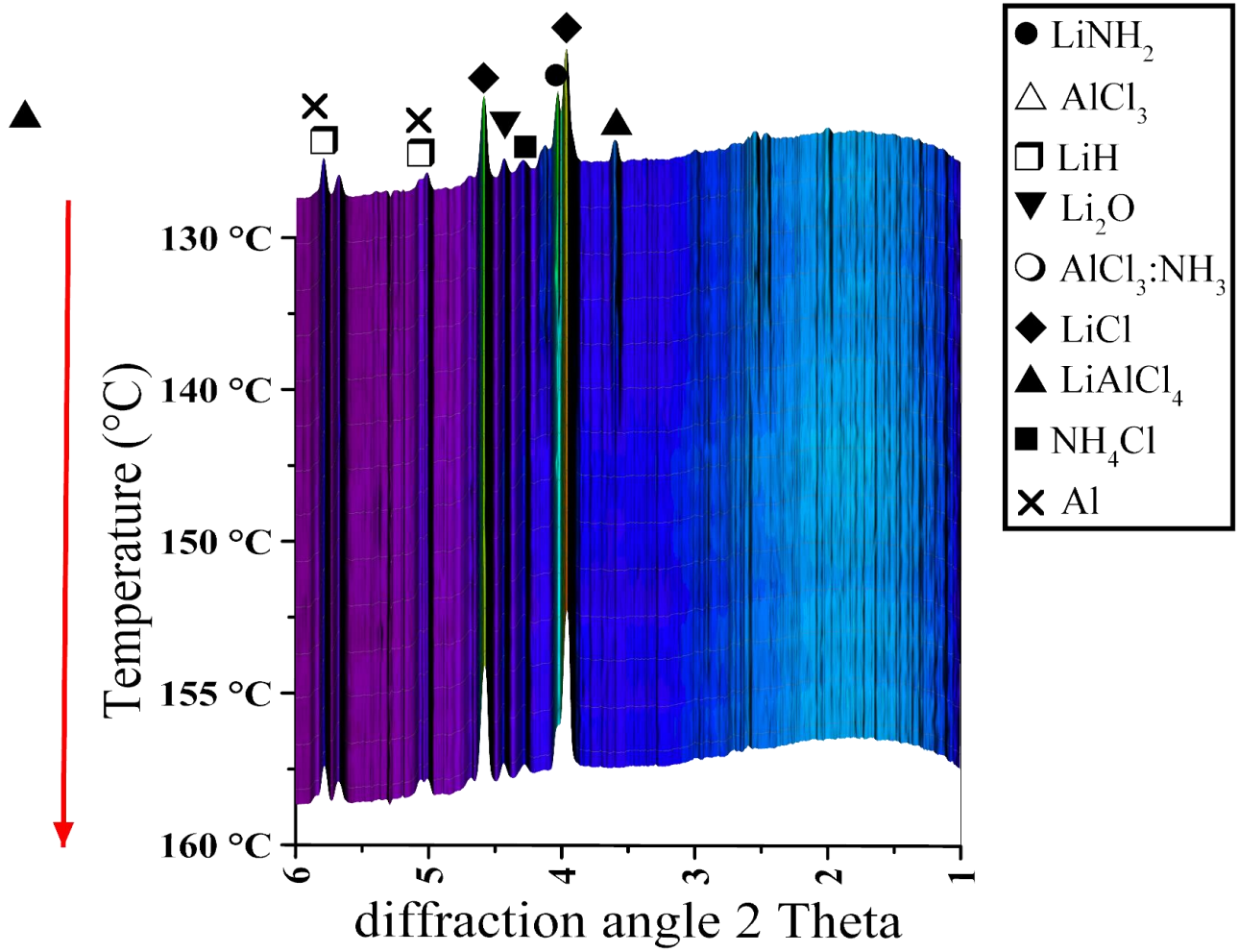


- $LiNH_2$
- $AlCl_3$
- LiH
- Li_2O
- $AlCl_3$:NH_3
- LiCl
- $LiAlCl_4$

$LiAlCl_4$

$LiCl + AlCl_3 \rightarrow LiAlCl_4$

SR-XPRD



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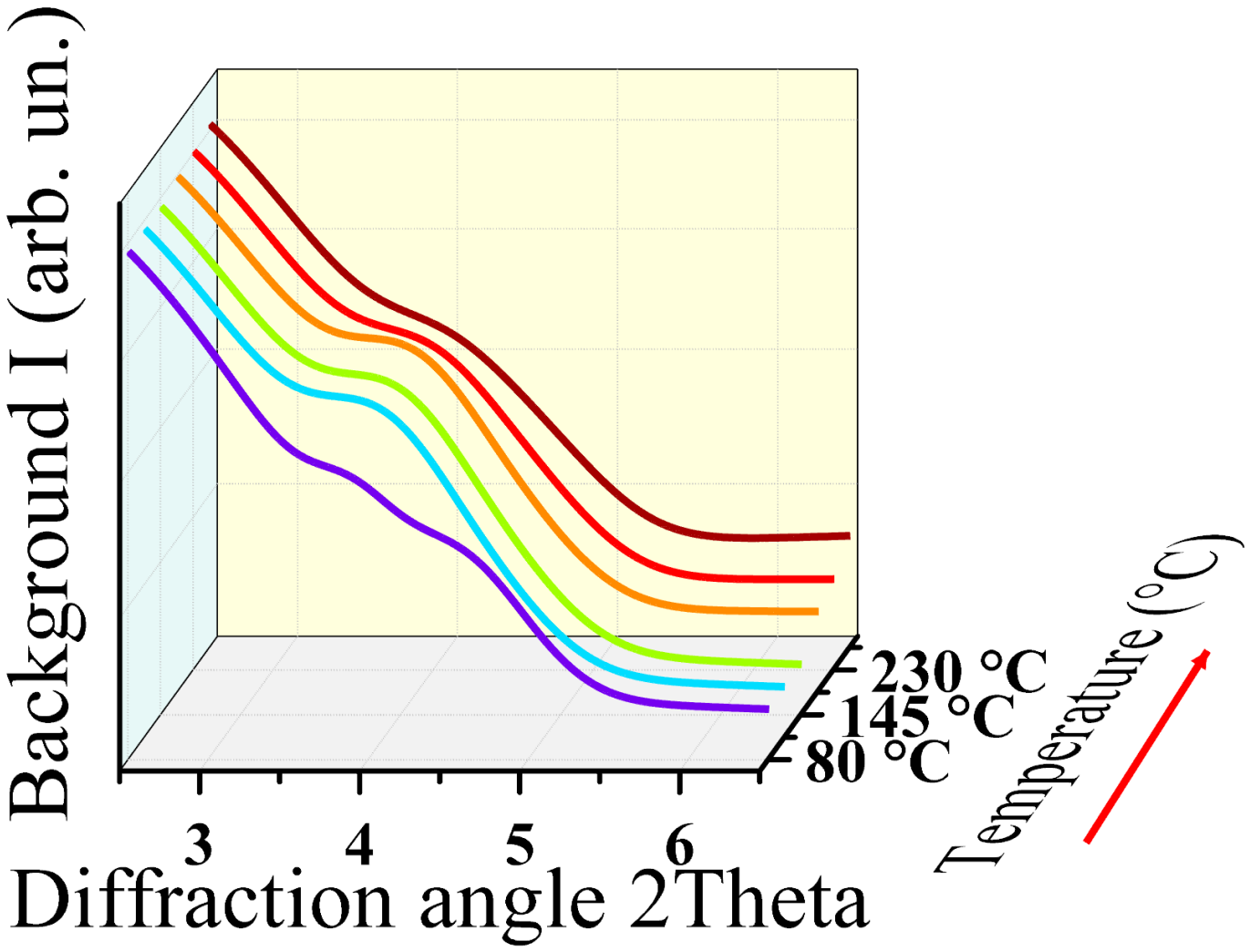
SR-XPRD



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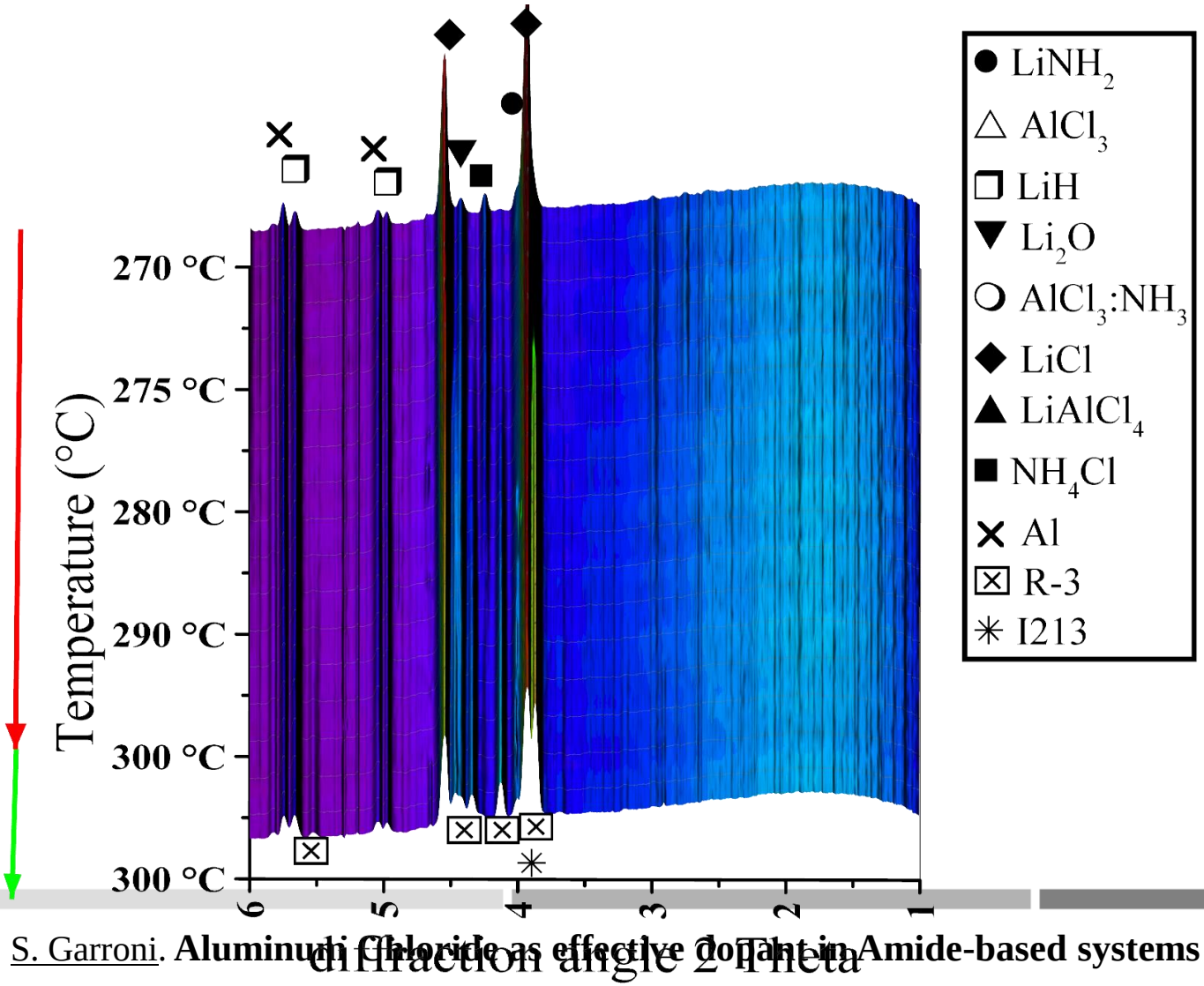
SR-XPRD


Temperature (°C)
270 °C
275 °C
280 °C
290 °C
300 °C
300 °C
6
5
4
3
2
1
diffraction angle 2 theta
LiNH2
AlCl3
LiH
Li2O
AlCl3:NH3
LiCl
LiAlCl4
NH4Cl
Al
R-3
I213