The French Research network on Hydrogen energy

FRH2 22-26/05/2023 Saint Gilles, La Réunion

Structural and thermodynamic study of $LaY_{2.3}Ni_{11.5-x}Mn_x$ compounds with $0.3 \leq x \leq 1.8$

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Context of the thesis

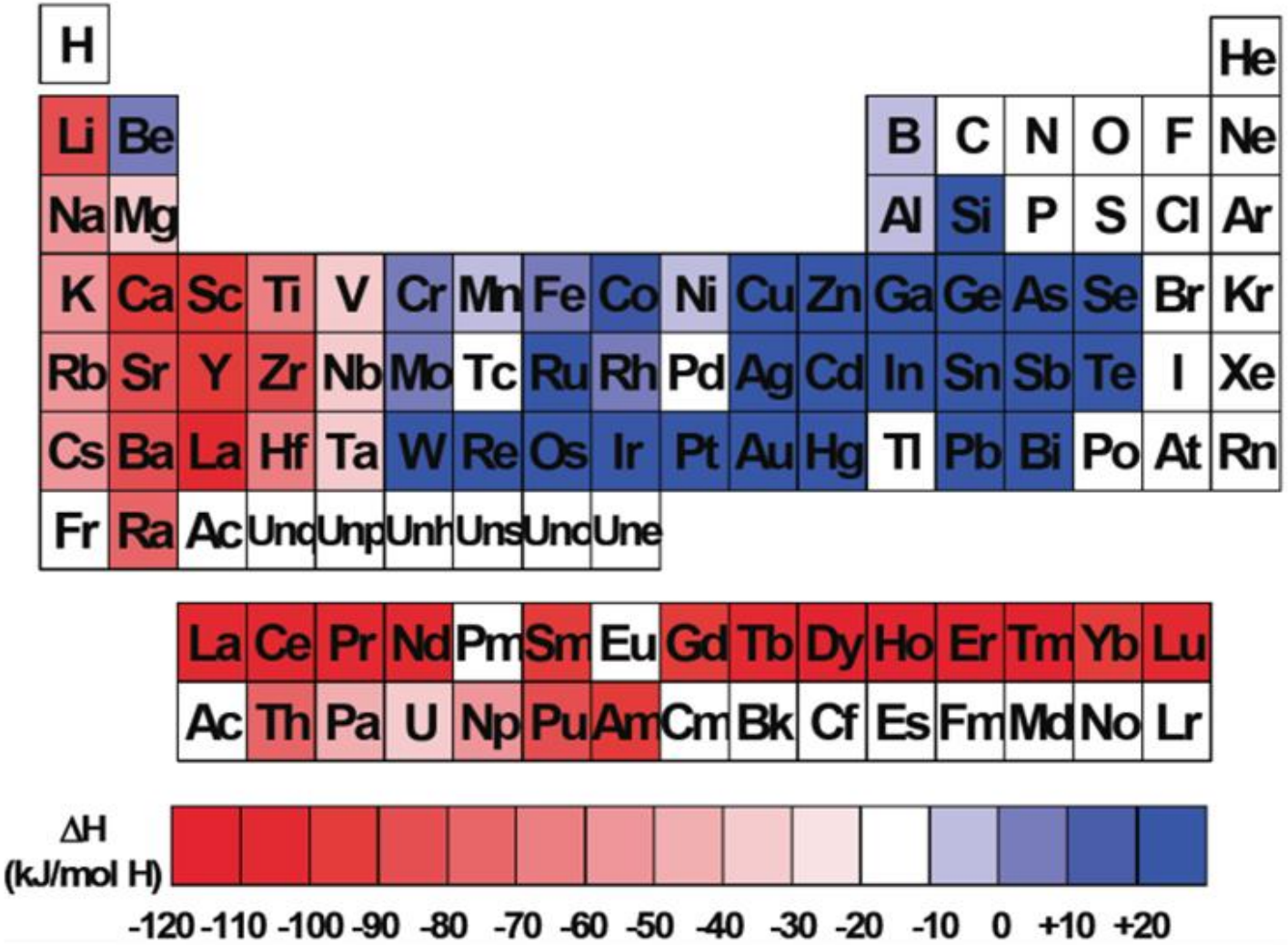
“New intermetallic intergrowth compounds for hydrogen storage under ambient conditions”

The idea is to develop new ***AB_n*** compounds (***A***=Y, Lanthanides and ***B***=Ni, Mn, Al, Fe) with a **high storage capacity**, **complete reversibility** and **good stability for applications under ambient conditions.**

Substitutions will be made on both ***A*** and ***B*** elements in order to improve the reversibility and to have a unique plateau at a low pressure.

➔ Objective: to develop new AB_n compounds with **a storage capacity ≥ 2 wt.% under ambient conditions** (T = 25°C–70°C and P ≤ 1 MPa) and a **complete reversibility.**

Context of the thesis



Elements *A*: stable hydrides at ambient T and P.

Elements *B*: unstable hydrides at ambient T and P.

***AB_n* compounds**:

➔Absorption and desorption at ambient T and P.

AB_2*, …, *AB_3*, *A_2B_7*, *A_5B_{19}*, …, *AB_5

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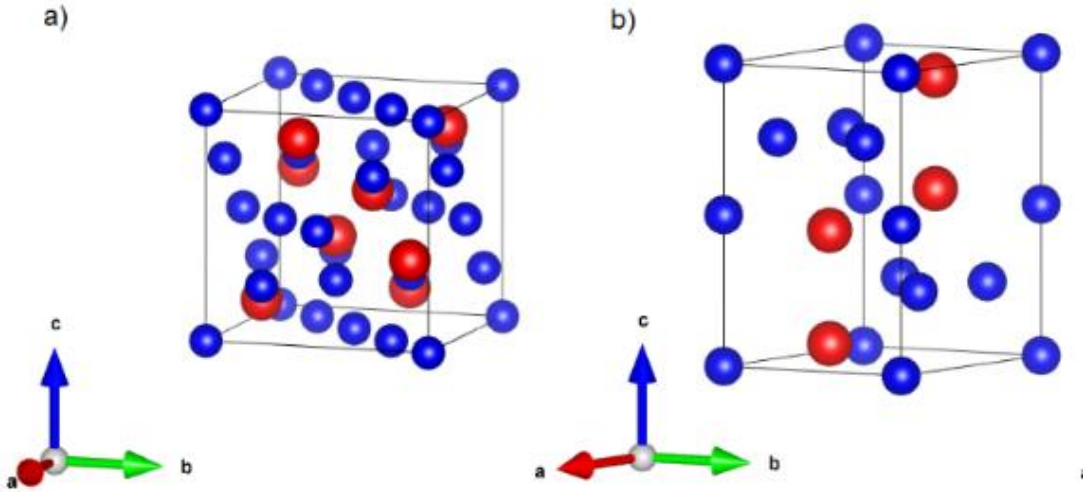
Context of the thesis

AB_2 and AB_5 compounds

Laves phases

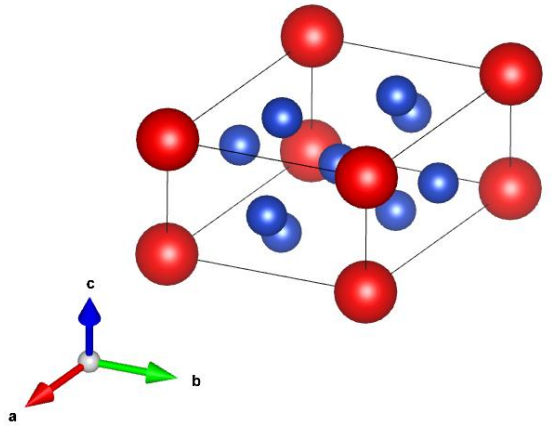


***C*14**: *P6$_3$/mmc*, hexagonal $MgZn_2$ structure type

***C*15**: *Fd$\bar{3}$m*, fcc $MgCu_2$ structure type

➔ These compounds have high hydrogen storage capacities but poor reversibility.

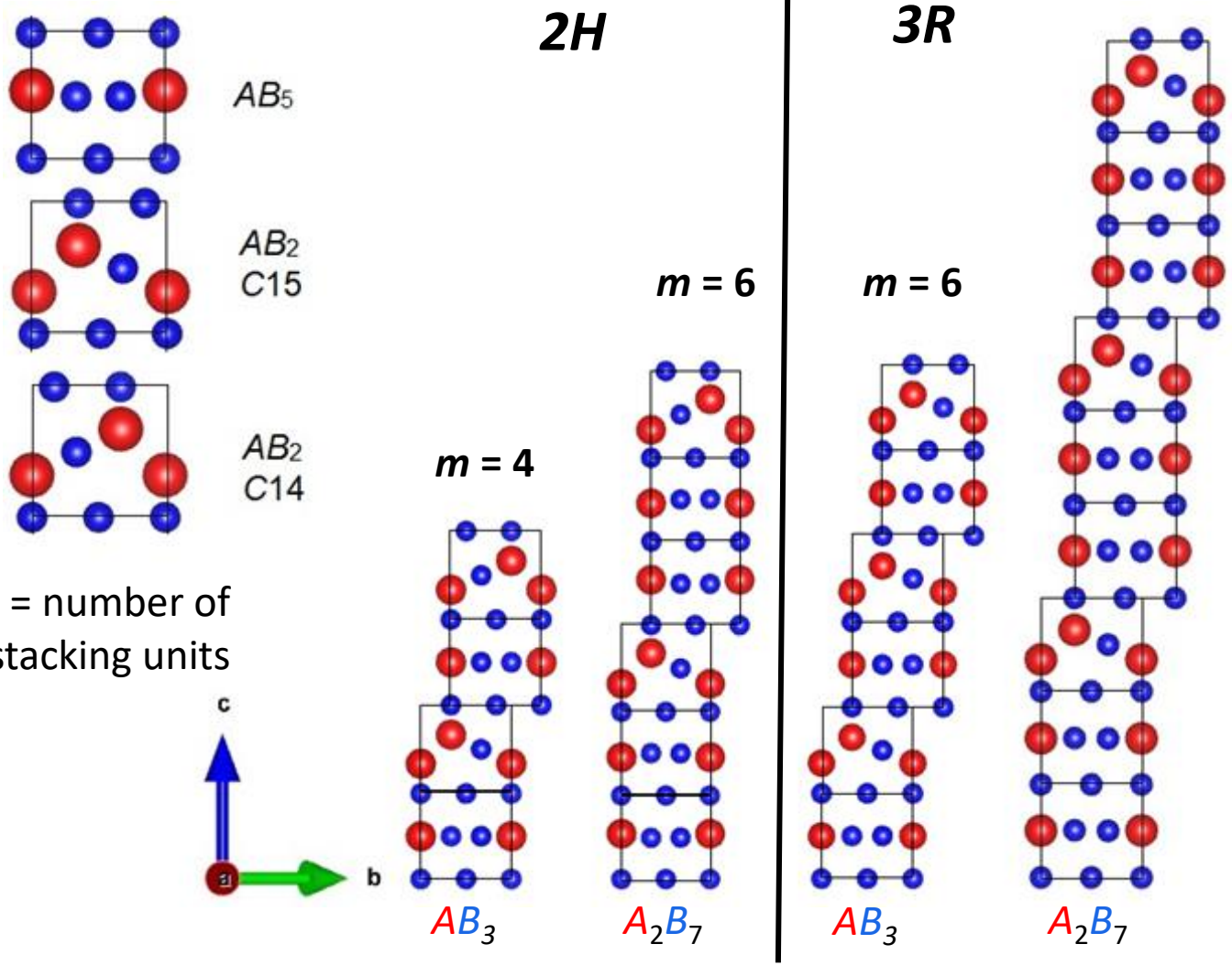
Haucke phases



P6/mmm, hexagonal $CaCu_5$ structure type

➔ These compounds have good hydrogen storage capacities (slightly lower than AB_2) and good reversibility.

Context of the thesis



The stacking structures of AB_n compounds ($2<n<5$)

$AB_n = z\,[A_2B_4] + y\,[AB_5]$

$z = 1$, $y = 1$ for AB_3

$z = 1$, $y = 2$ for A_2B_7

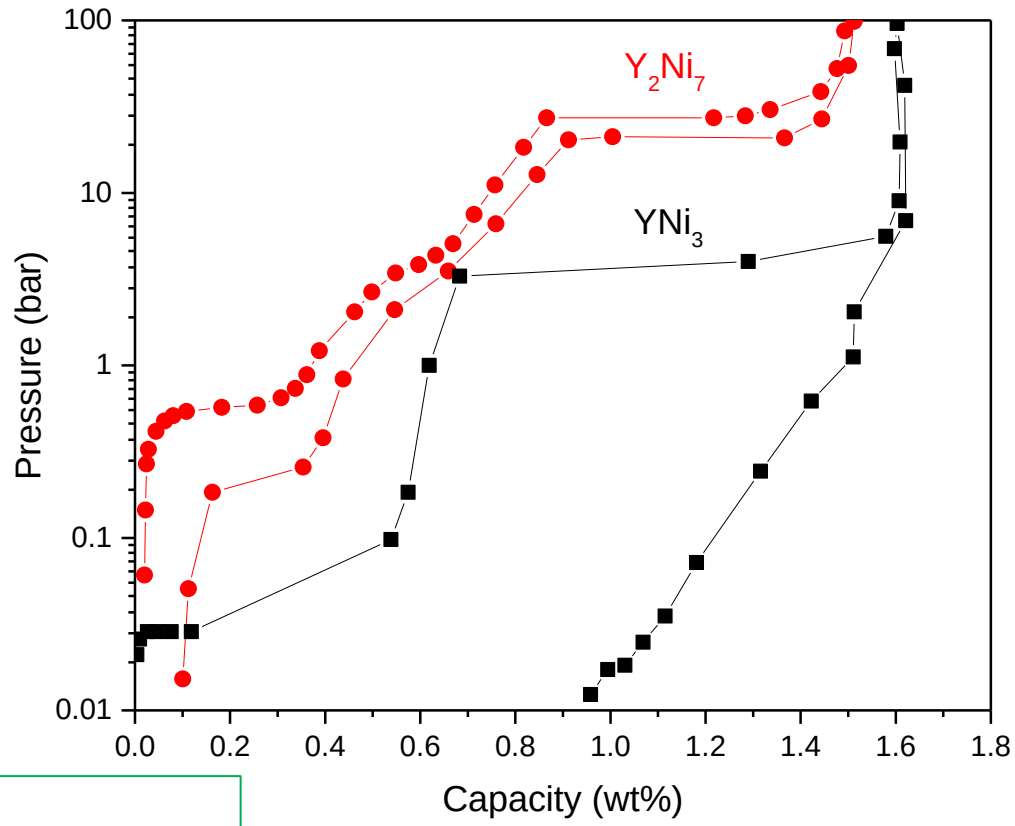
V^* (average volume) = V/m
V: Cell volume
m = number of stacking units

c^* (average lattice parameter) = c/m
c : Lattice parameter
m = number of stacking units

Context of the thesis

AB_3 and A_2B_7

- **A binary AB_3 compound (YNi_3[1])**
  - 1st plateau at a low pressure.
  - Good storage capacity.
  - 2 plateaus at different pressures
  - Not reversible.
- **A binary A_2B_7 compound (Y_2Ni_7[2])**
  - 1st plateau at a higher pressure.
  - Lower storage capacity.
  - 3 plateaus at different pressures
  - Good reversibility.



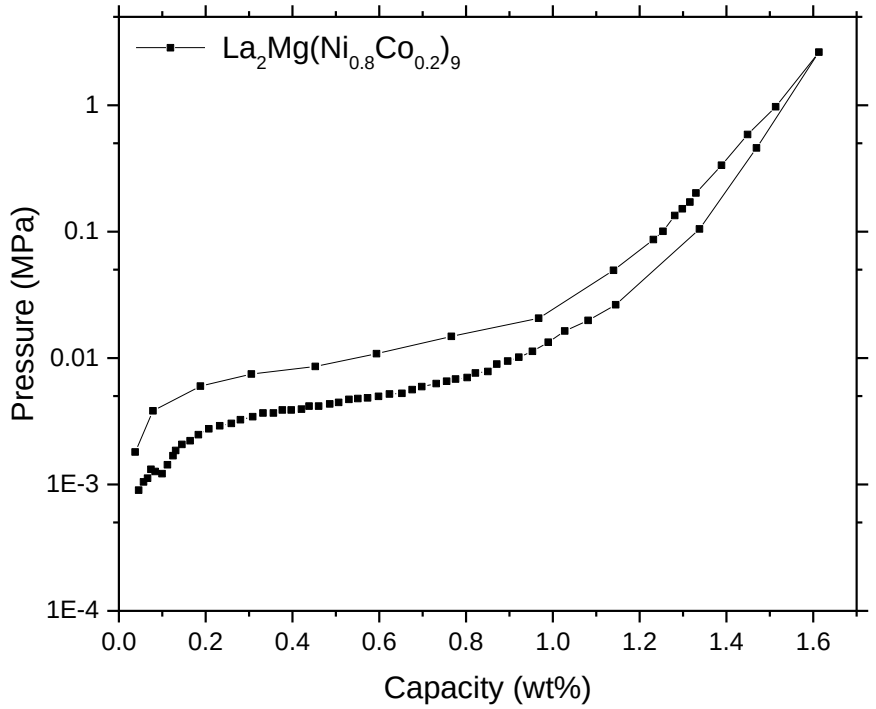
The goal ?
➔To have a compound with :
-A high storage capacity.
-A good reversibility.
-A unique plateau

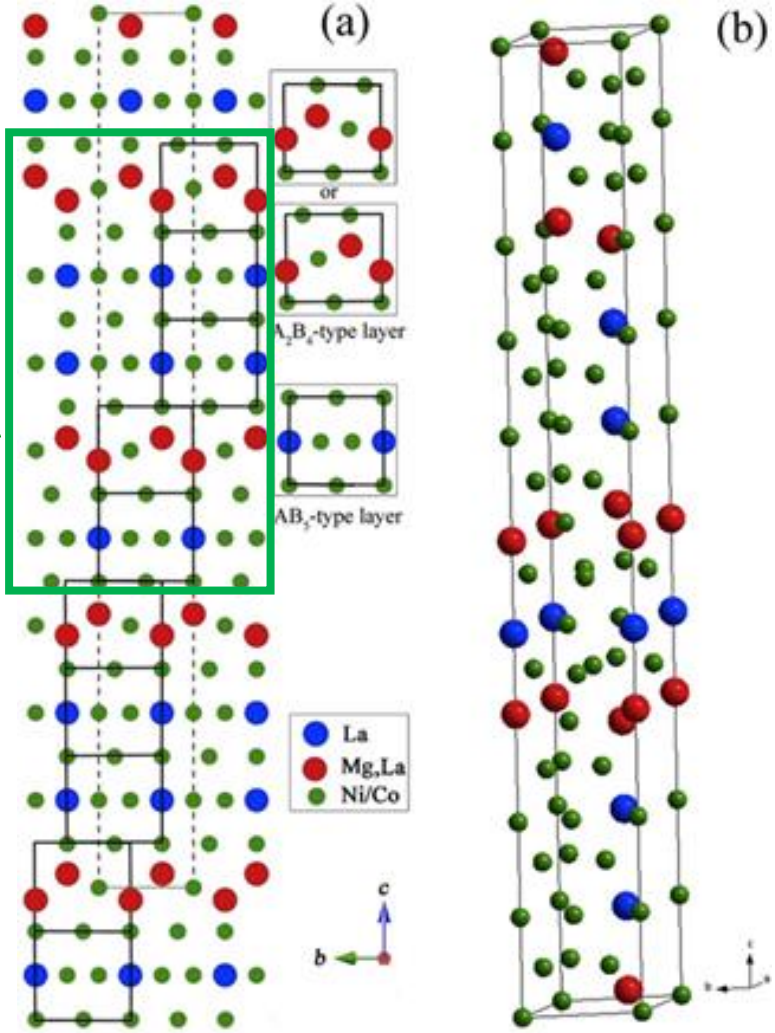
[1] N. Madern *(**2018**), PhD thesis.*
[2] V. Charbonnier *(**2015**), PhD thesis.*

Context of the thesis

A_7B_{23}: $La_{17.2}Mg_{6.6}Ni_{60}Co_{16.2}$

- La-Mg-Ni-Co[3]
- $[AB_5]$-$[A_2B_4]$-$[AB_5]$-$[AB_5]$-$[A_2B_4]$ ➔ $3[AB_5]+2[A_2B_4]= A_7B_{23}$





[3] Y. Li *et al* (***2018***) *J. Power Sources, 441, 126667.*

Syntheses method

6 $\boldsymbol{AB_{3.48}}$ compounds (*A* = La+Y; *B* = Ni+Mn) based on $LaY_{2.3}Ni_{11.5-x}Mn_x$ **(*x* = 0.3; 0.6; 0.9; 1.2; 1.5; 1.8)**

Arc-melting (3g)

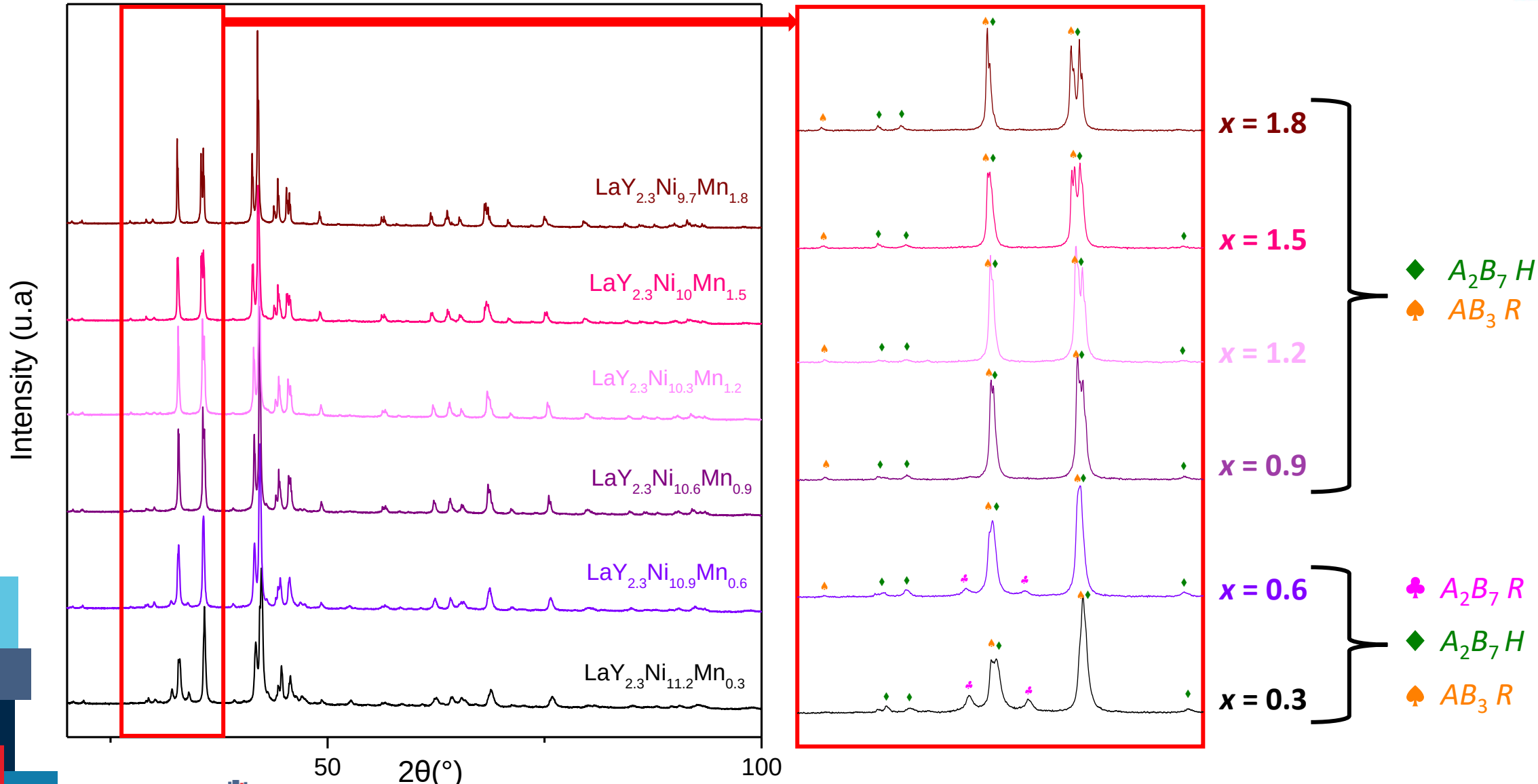
➔Re-melted 4 times

Sample sealed under argon

➔Annealed at 900°C for 3 days.

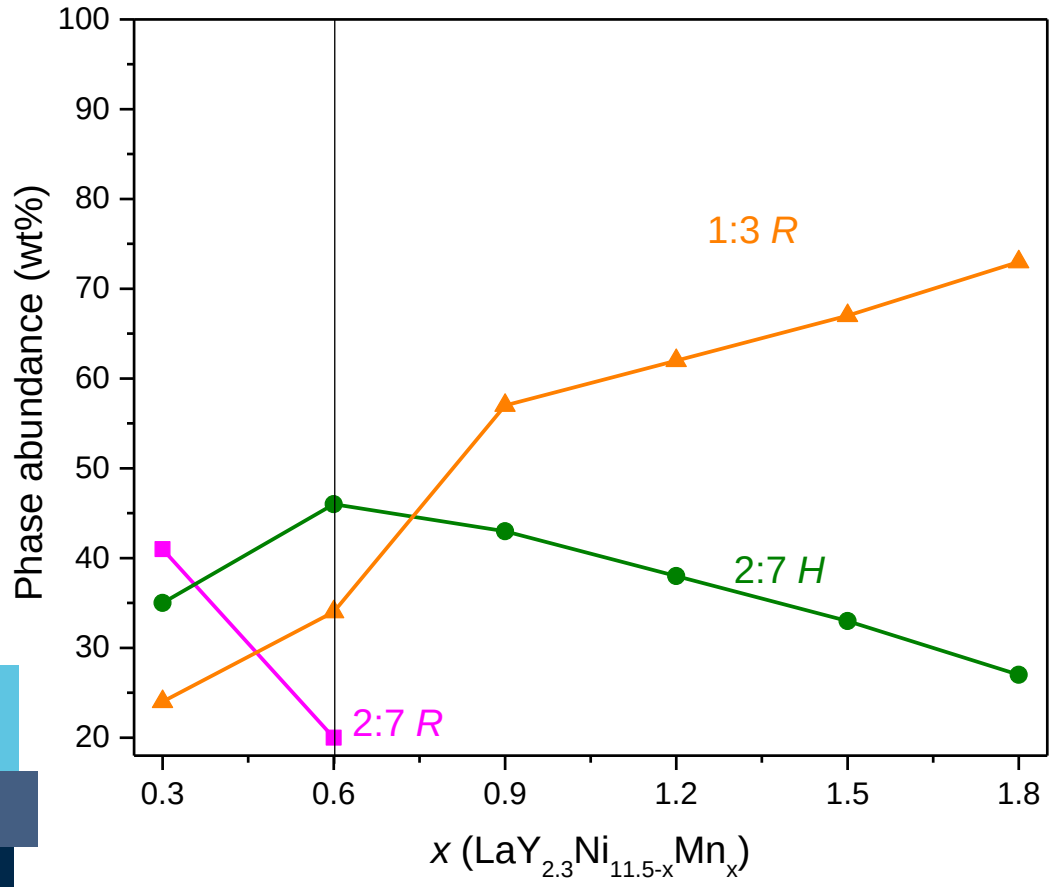
Annealing furnace

Structural characterization by XRD



Compilation of the Rietveld refinement results

❑ **Phases percentages:**



Mn content		**Phase abundance**
0.3 to **0.6**	→	wt% AB_3R and A_2B_7H ↗ wt% A_2B_7R ↘
0.9 to **1.8**	→	wt% AB_3R ↗ wt% A_2B_7H ↘

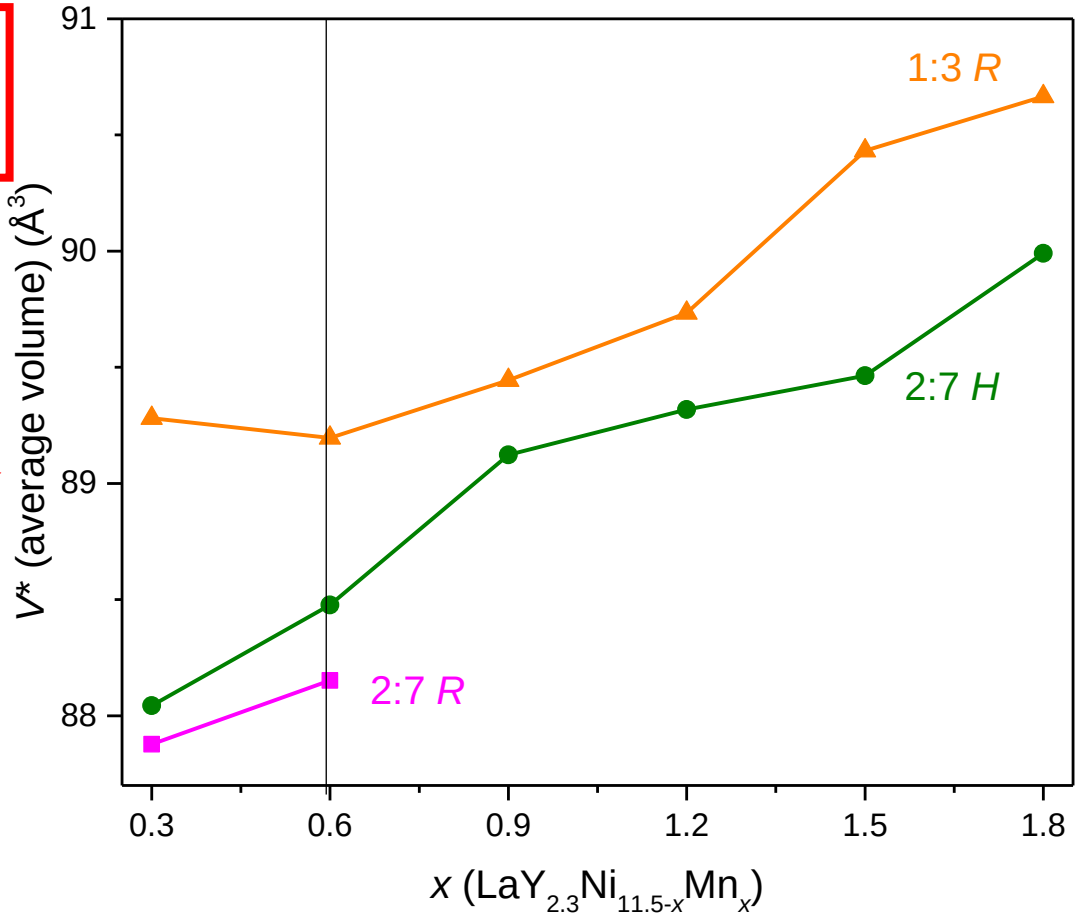
Mn (at%)	0.3	0.6	0.9	1.2	1.5	1.8
A_2B_7R (wt%)	41	20	0	0	0	0
A_2B_7H (wt%)	35	46	43	38	33	27
AB_3R (wt%)	24	34	57	62	67	73

→ wt% AB_3R ↗
wt% A_2B_7 $(H+R)$ ↘ with Mn content

Compilation of the Rietveld refinement results

❑ Cell volume:

V (average volume) = **V**/**m***
V: Cell volume
m = number of stacking units



Increasing the Mn content increases the *V of all the phases.**

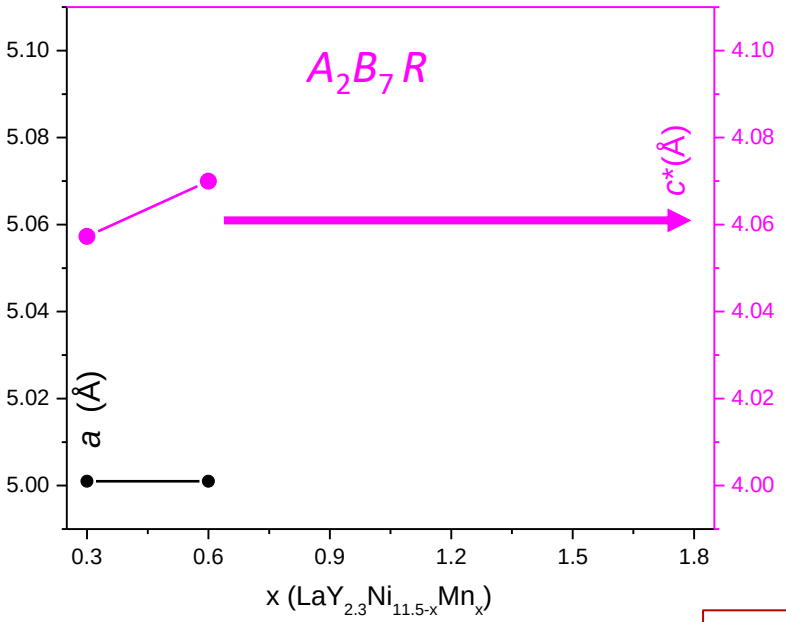
Exception:
Mn (**0.3** to **0.6**) ➔ $V^*(AB_3\ R)$ ↘

➔ Which positions does the Mn occupy in these structures ?

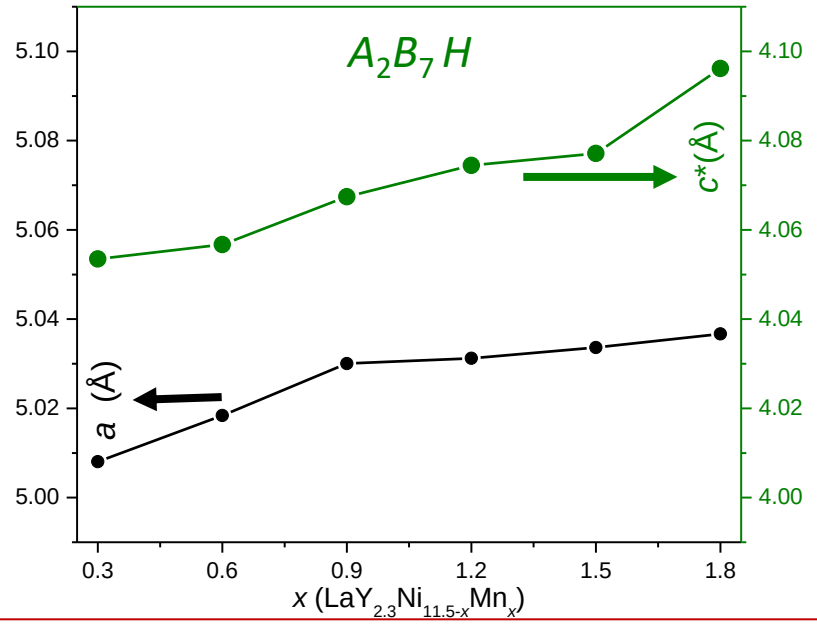
Compilation of the Rietveld refinement results

❑ Lattice parameters of each phases:

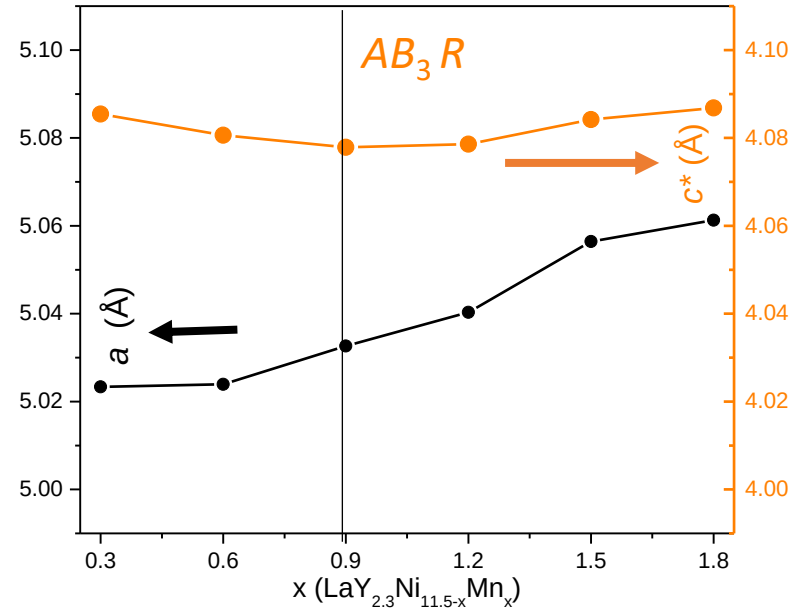
Mn (**0.3** to **0.6**) ↗ ➔ «c^*» ↗



Mn (**0.3** to **1.8**) ↗ ➔«*a*» and «c^*» ↗



Mn (**0.3** to **0.9**) ↗ ➔ «*a*» ↗ *and* «c^*» ↘



Lattice parameters expansion ➔ geometrical effect

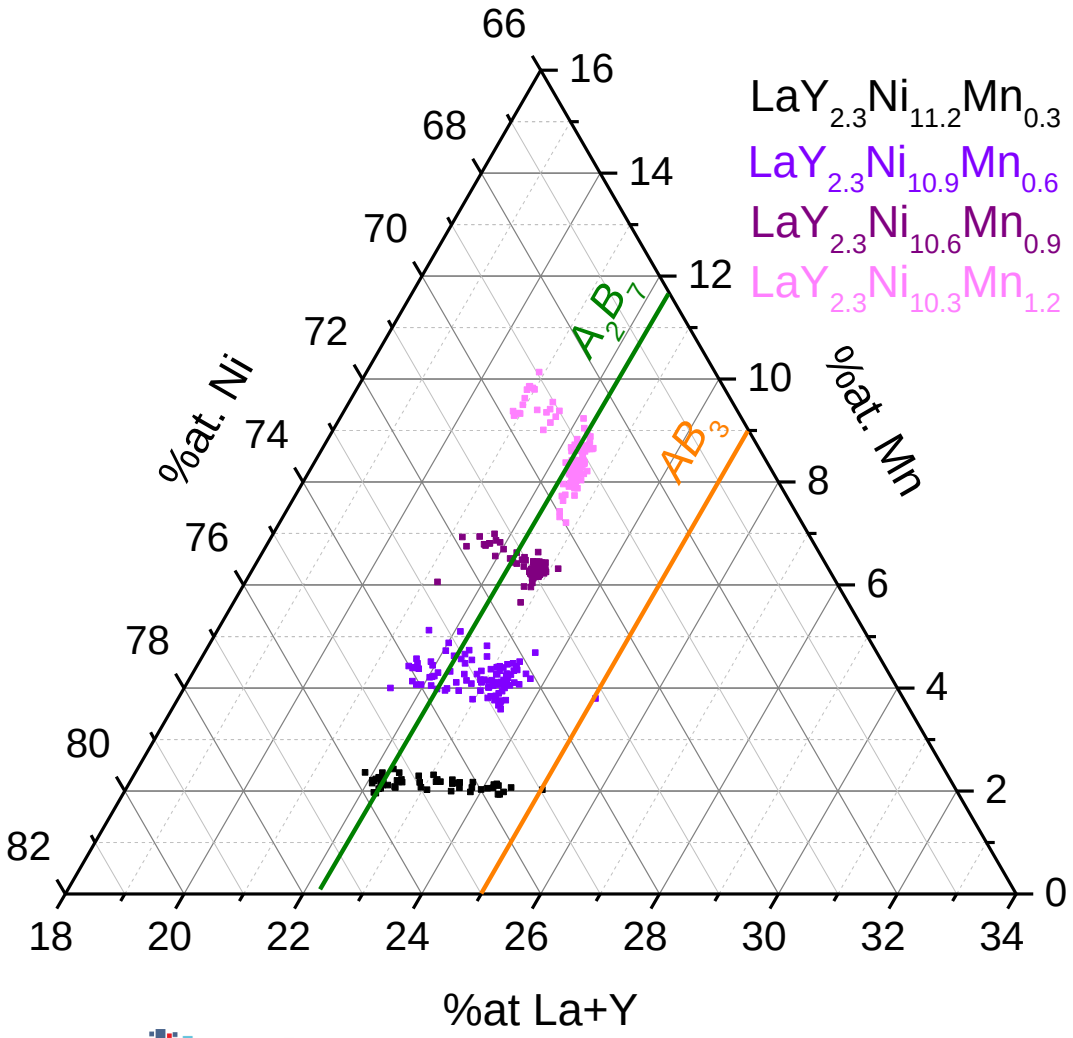
Mn (1.3 Å) occupies Ni's positions (1.24 Å) in the unit $[AB_5]$[4].

Unusual evolution of c^*
Mn can also occupy both "*A*" Y (1.8 Å) La (1.87 Å) and "*B*" positions in the unit $[A_2B_4]$[5].

c** (average lattice parameter) = *c*/*m
c : Lattice parameter
***m* = number of stacking units**

[4] C. Lartigue *et al, (**1980**). J. Less-Common Met, 75, 23-29.*
[5] H. Shen *et al, (**2023**). J. Alloys Compd, 952, 169632.*

Chemical characterization by Electron Probe Micro Analysis (EPMA)



The local compositions of these four compounds (**$LaY_{2.3}Ni_{11.2}Mn_{0.3}$** **$LaY_{2.3}Ni_{10.9}Mn_{0.6}$** **$LaY_{2.3}Ni_{10.6}Mn_{0.9}$** et $LaY_{2.3}Ni_{10.3}Mn_{1.2}$) are positioned between the two phases AB_3 and A_2B_7.

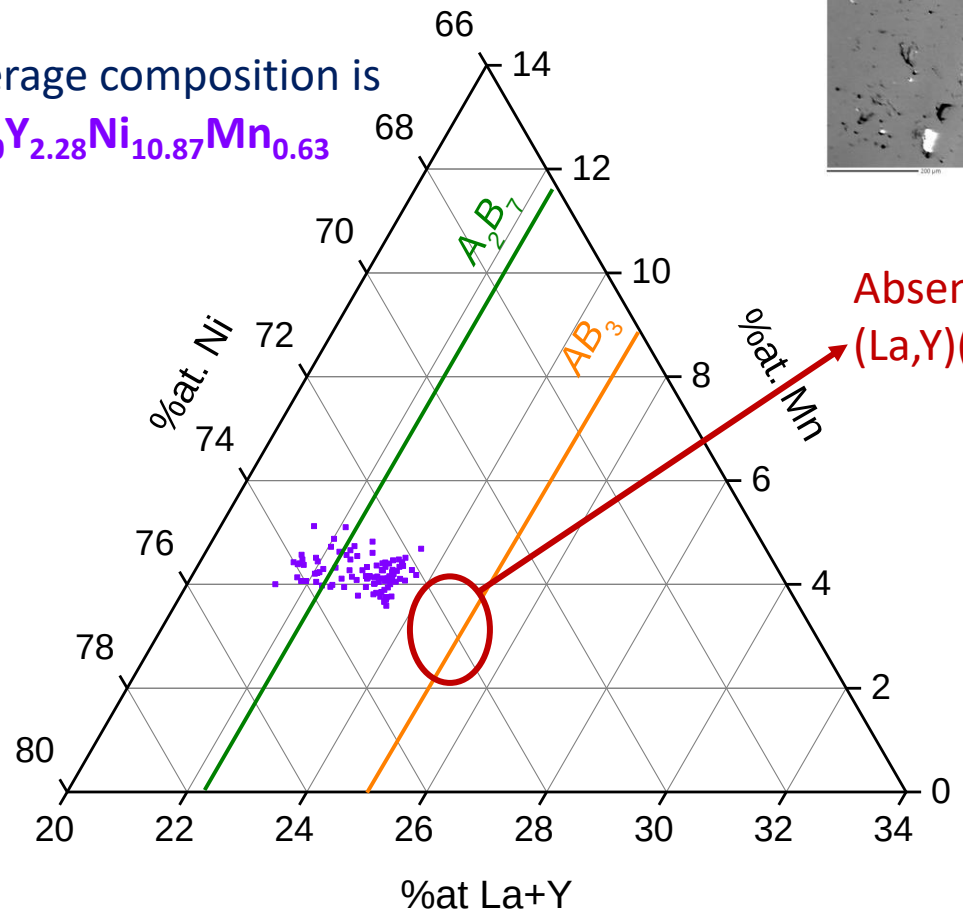
The stoichiometry of these compounds is **$AB_{3.48}$** (close to $AB_{3.5}$ (A_2B_7)) which explains the presence of the point clusters around the A_2B_7 line.

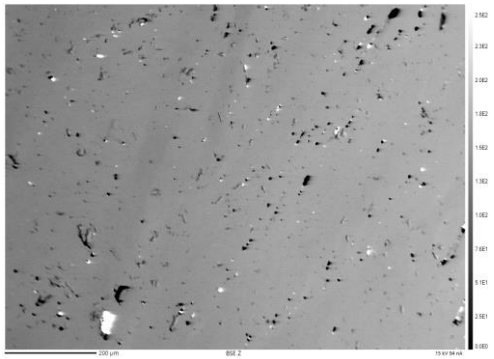
$LaY_{2.3}Ni_{10}Mn_{1.5}$ and $LaY_{2.3}Ni_{9.7}Mn_{1.8}$ are under way

Chemical characterization by Electron Probe Micro Analysis (EPMA)

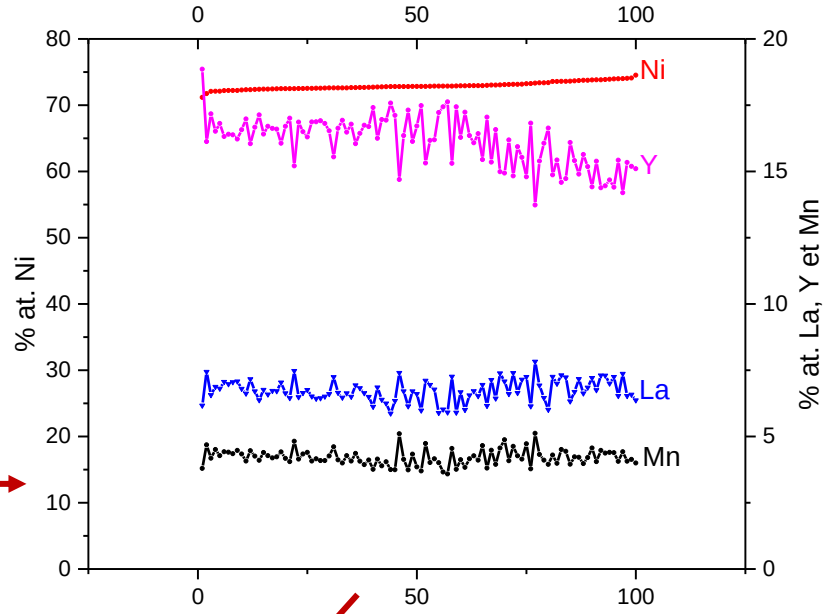
❑ $LaY_{2.3}Ni_{10.9}Mn_{0.6}$

The average composition is
$La_{1.00}Y_{2.28}Ni_{10.87}Mn_{0.63}$





Absence of the composition $(La,Y)(Ni,Mn)_3$ →

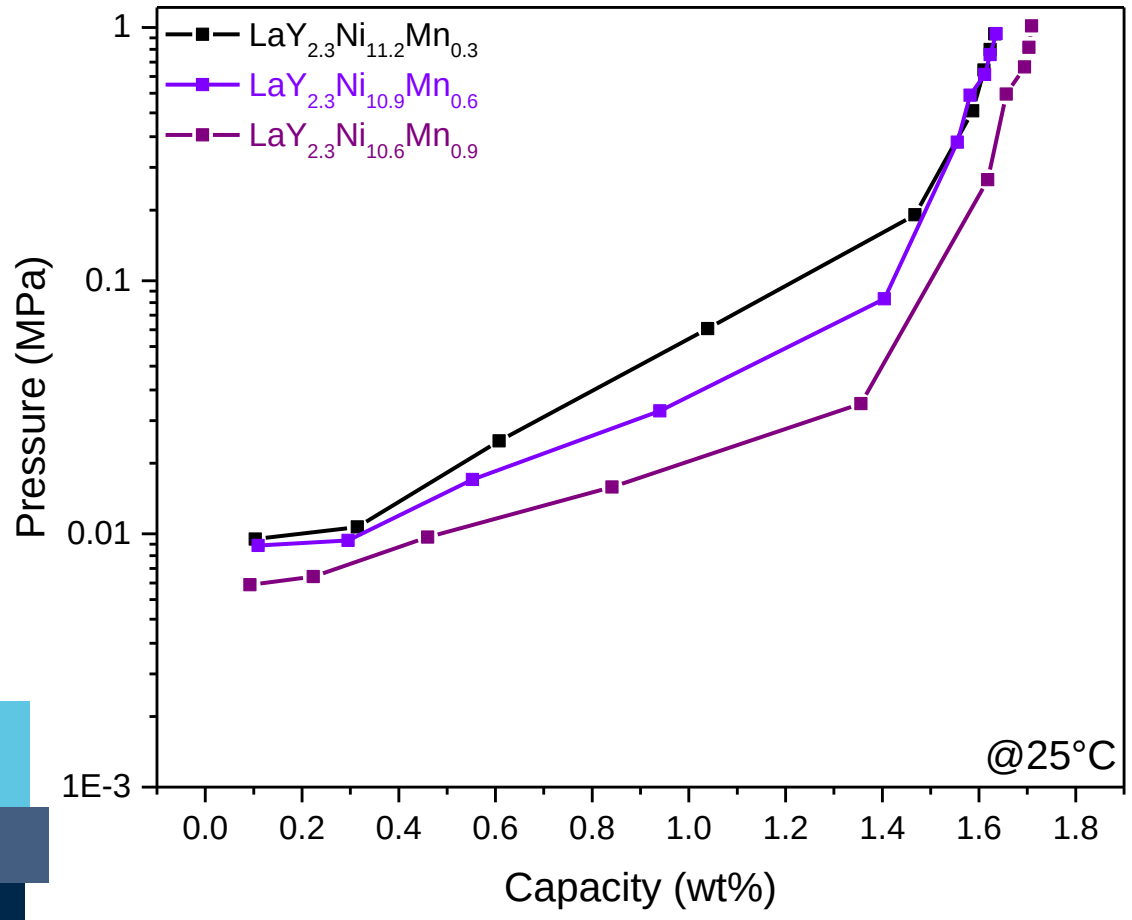


The variation of the **Y** (r =1.8 Å) content is the <u>exact opposite</u> of the variation of the **La** (r = 1.87 Å) and **Mn** (r = 1.27 Å) content.

<u>Hypothesis</u>: Mn could occupy "*A-atom*" positions of Y type in the unit AB_2[5] ➔ (La,Y,Mn) $(Ni,Mn)_3$

[5] H. Shen *et al, (**2023**). J. Alloys Compd, 952, 169632.*

Pressure Composition-Isotherm curves (PCI)



- **Activation process**: at 150°C for 2 hours under secondary vacuum.
- **PCI measurement**: at 25°C with a maximum applied pressure of 1 MPa.

The maximum recorded capacity at 25 °C and 1 MPa for :

- **$LaY_{2.3}Ni_{11.2}Mn_{0.3}$ is 1.63 wt%.**
- **$LaY_{2.3}Ni_{10.9}Mn_{0.6}$ is 1.63 wt%.**
- **$LaY_{2.3}Ni_{10.6}Mn_{0.9}$ is 1.71 wt%.**

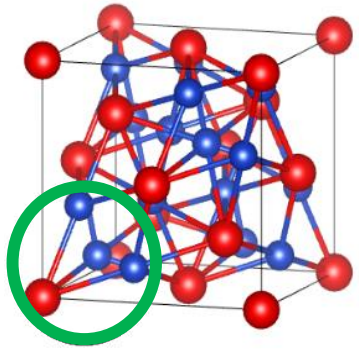
- The studied compounds present unique sloping plateaus.

➔ By playing on the chemical substitution with La and Mn, the multiple plateaus behavior is deleted.

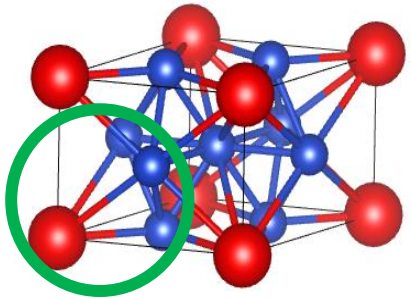
$LaY_{2.3}Ni_{10.3}Mn_{\mathbf{1.2}}$, $LaY_{2.3}Ni_{10}Mn_{\mathbf{1.5}}$ and $LaY_{2.3}Ni_{9.7}Mn_{\mathbf{1.8}}$ are under way

Pressure Composition-Isotherm curves (PCI)

$[A_2B_4]$

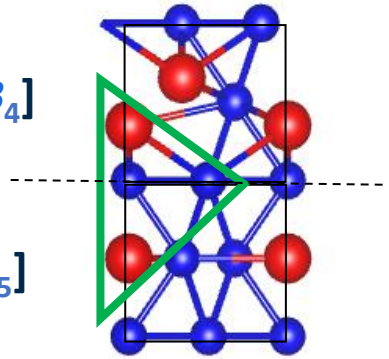


$[AB_5]$



$[A_2B_4]$

$[AB_5]$

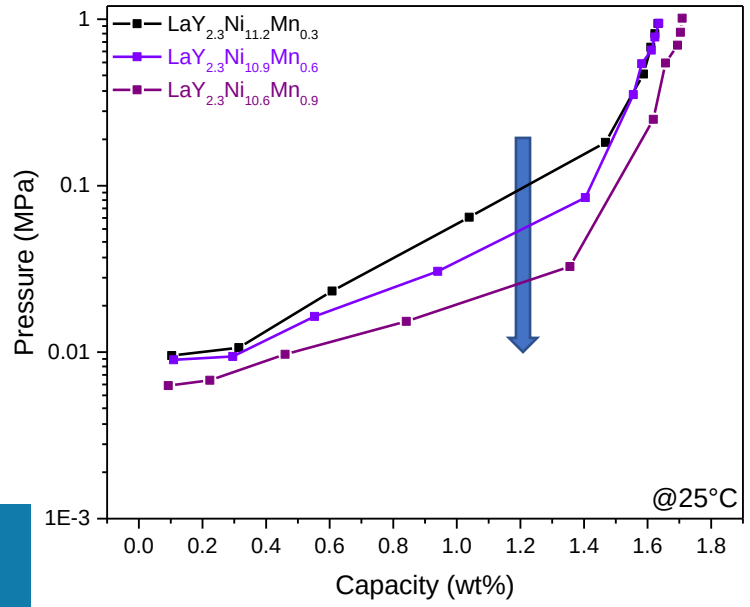


1 elemental brick of AB_3

Atom	Environment	C14	C15
		Site	
H	T-A2B2	12k	96g
H	T-AB3	4f	32e
H	T-B4	4e	8b

Atom	Environment	Site
H	T-B4	4*h*
H	O-A2B2	6*m*
H	T-AB3	12*n*
H	T-AB3	12*o*

Atom	Environment	Site
H	T-A2B2	$18h_1$
H	T-A2B2	$18h_2$

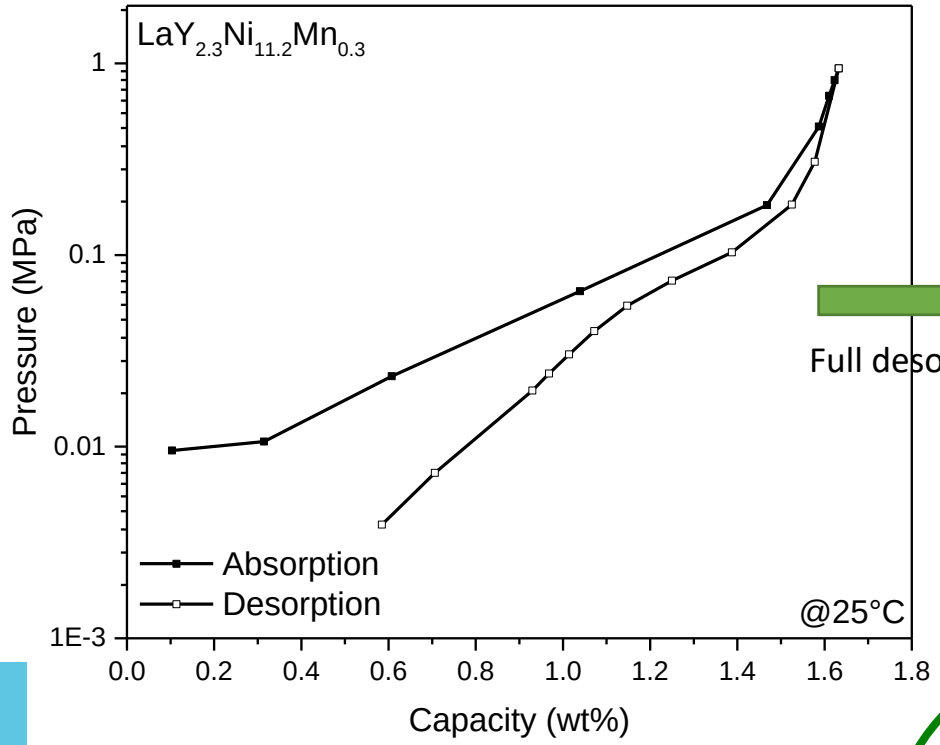


- Increasing the Mn content in these compounds lowers the plateau pressure and flattens it.

➔ **Hypothesis :** Expanding the phases' volume as seen in the XRD results increases the size of available interstitial sites (previously needing a higher H_2 pressure to be occupied).

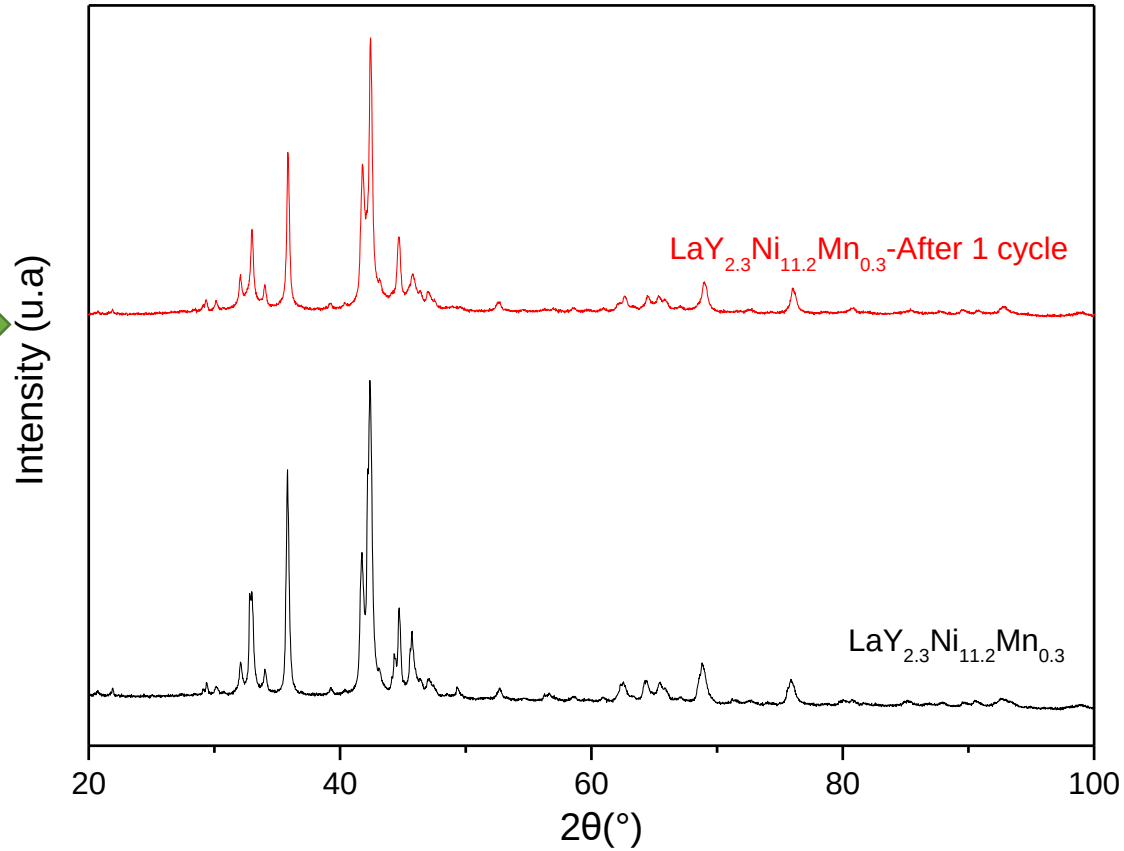
Pressure Composition-Isotherm curves (PCI)

❑ **XRD results after one cycle of hydrogenation/dehydrogenation of $LaY_{2.3}Ni_{11.2}Mn_{0.3}$:**



XRD

Full desorption at **150°C over night under vacuum.**



After 1 cycle of absorption/desorption, the **$LaY_{2.3}Ni_{11.2}Mn_{0.3}$** compound preserves its structure ➔ completely reversible.

Conclusion

- We synthesized 6 multi-phased compounds $\mathbf{LaY_{2.3}Ni_{11.5-x}Mn_x}$ with different Mn contents ($\mathbf{0.3 \leq x \leq 1.8}$) containing the phases AB_3 and A_2B_7 with different percentages.
  - ✓ Mn substitution leads to a unique plateau pressure.

- The effects of increasing the Mn content:
  - ✓ Mn favors the formation of AB_3 phase.
  - ✓ Mn can occupy "*A*" and "*B*" sites. (Which ones exactly?)
  - ✓ Mn lowers the plateau pressure. (How?)

- Good storage capacities: up to **1.7 wt%** at **1 MPa** and **25°C** and complete reversibility.

Outlooks

1. Neutron diffraction measurements will be conducted to identify the exact positions of Mn in our structures.
2. Continue studying the thermodynamic properties + cycling.

This work was funded by the French National Research Agency (ANR), reference project "ANR-22-PEHY-0007", as part of the France 2030 program.

Thank you for your attention