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Improvement of reversible H storage capacity by fine tuning of the composition in the pseudo-binary systems $A_{2-x}La_xNi_7$ ($A = Gd, Sm, Y, Mg$)

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Key Word: Hydrogen storage, crystal structure, thermodynamic tuning

Abstract

A_2B_7 compounds ($A =$ rare earth or Mg, $B =$ transition metal) are widely studied as active materials for negative electrode in Ni-MH batteries. By playing on the substitution rate of both A and B elements, it is possible to prepare various compositions. This strategy will help to improve the properties, for example get a higher reversible hydrogen capacity and a well-adapted hydrogen sorption pressure. Indeed, A can be almost all light rare earths (La to Gd), yttrium and alkaline earth metals (Mg or Ca), whereas B can contain various late transition metals (Mn to Ni). To understand the effects of composition on the physicochemical properties of La_2Ni_7 -based compound, various pseudo-binary systems have been investigated: $Gd_{2-x}La_xNi_7$ ($x = 0, 0.6, 1, 1.5$), $Sm_{2-x}La_xNi_7$ ($x = 0, 0.5, 1, 1.5$), $Y_{2-x}La_xNi_7$ ($x = 0, 0.4, 0.5, 0.6, 0.8, 1, 1.5, 1.75$) and $A_{0.5}La_{1.1}Mg_{0.4}Ni_7$ ($A = Sm, Gd$ and Y). To determine their crystallographic properties, X-ray diffraction analysis was performed followed by Rietveld refinement. Thermodynamic properties regarding reversible hydrogen sorption were investigated at room temperature. Quaternary compounds present drastically improved sorption properties in the frame of practical energy storage applications with reversible capacity equivalent to 400 mAh/g for the compound $La_{1.1}Sm_{0.5}Mg_{0.4}Ni_7$.

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1 Introduction

The consuming of fossil fuels is not only the main cause of air polluting but also the origin of global warming with more and more alarming consequences. These leads to serious consideration of use of alternative energies: solar, wind and sea waves. Those energies require energy storage for final consuming. Hydrogen is one candidate either can be used as fuel[1–3] or charge carrier in Ni-MH batteries[4–6].

AB_5 compounds (A = rare earth, B = transition metal) are commonly used as negative electrode materials in commercial Ni-MH batteries [4,6,7]. To act as a good anode material, those compounds must exhibit specific thermodynamic properties. First, they must be able to absorb reversibly a large quantity of hydrogen through a large equilibrium plateau pressure. Second, this plateau must lay in the practical electrochemical window located in the pressure range between 0.001 and 0.1 MPa at room temperature [5].

The typical gravimetric capacity obtained with those AB_5 compounds reaches around 300-350 mAh/g [5,8,9]. To increase this specific capacity, new systems involving new chemistry are being considered. Indeed, AB_y compounds ($2 < y < 5$) are studied worldwide [9–12]. They can be described as stacking structures made of $[A_2B_4]$ and $[AB_5]$ subunits piled along the c crystallographic axis. Their general formula, introduced by Khan [13], can be written as: $y = \frac{5n+4}{n+2}$ (where n is the number of $[AB_5]$ subunits). For A_2B_7 , n equals 2 and consequently, the basic period can be written as $2 \cdot [AB_5] + [A_2B_4]$. Those phases are polymorphs as they crystallize either in rhombohedral ($3R$) - Gd_2Co_7 -type - or hexagonal ($2H$) symmetry - Ce_2Ni_7 -type .

Binary compounds Gd_2Ni_7 , Y_2Ni_7 , Sm_2Ni_7 and La_2Ni_7 were previously studied [14,15][16] regarding their ability to form hydrides. These binary compounds absorb large amounts of hydrogen but exhibit several plateaus (two for Gd_2Ni_7 , Sm_2Ni_7 and La_2Ni_7 ; three for Y_2Ni_7), which is not suitable for application. This behavior is mainly caused by the stacked structure and the mismatch between subunits $[A_2B_4]$ and $[AB_5]$. This mismatch is also responsible for the hydrogen induced amorphization (HIA) of these compounds. Since the atomic size of rare earths play an important role on this geometrical parameter, it is interesting to study the effect of different rare earths on the hydrogenation properties.

In the present paper, we study the effect of lanthanum and/or magnesium substitution to the rare earths $A = Gd, Sm$ or Y in A_2Ni_7 compounds. Atomic radius r_A of La (1.87 Å) is larger than that of gadolinium (1.787 Å), samarium (1.804 Å) and yttrium (1.776 Å). Lanthanum can occupy the A site either in the $[AB_5]$ or in the $[A_2B_4]$ subunits. This substitution generates an adjustment of the mismatch between the two subunits and thus influences the hydrogenation properties. On the other hand, magnesium (1.599 Å) is also large enough to substitute lanthanides or yttrium, but it only occupies the A site in the $[A_2B_4]$ subunits [17,18]. It plays a key role in decreasing the $[A_2B_4]$ subunit volume and stabilizing the structure toward HIA by reducing the atomic radius ratio r_A/r_B [19]. Furthermore, being much lighter, magnesium leads to much higher specific weight capacity.

Herein the series $A_{2-x}La_xNi_7$ and $La_{1.1}A_{0.5}Mg_{0.4}Ni_7$ ($A = Gd, Sm$ or Y) have been synthesized and studied in terms of crystallographic and thermodynamic properties.

2 Experimental

The compounds were synthesized from high purity elements (Gd (Alfa Aesar 99.9%), La (Alfa Aesar 99.9%), Mg (Alfa Aesar 99.8%), Ni (Praxair 99.95%), Sm (Alfa Aesar 99.9%) and Y (Santoku 99.9%)). For the compounds without samarium and/or magnesium, the elements were melted stoichiometrically in an induction furnace. To ensure good homogeneity, this step was repeated five times. The obtained ingots were wrapped in a tantalum foil and annealed for one week under argon atmosphere in a silica tube at 1000 °C. The compounds containing samarium were synthesized with a 2-5 wt.% excess of samarium to anticipate metal evaporation. After induction melting, the ingot was crushed into powder (<100 μm). It was pressed into a 2 g-pellet, wrapped in a tantalum foil and annealed under argon atmosphere in a sealed stainless steel crucible for 3 days at 950 °C. For the compounds containing magnesium, a precursor made of rare earths and nickel was first prepared by induction melting. The obtained ingot was crushed into powder (<100 μm). Magnesium powder (<44 μm) was then added with small excess to the mixture. The final powder was pressed into a 2 g-pellet, which was annealed following the same procedure as for samarium-containing compounds.

All samples were characterized by X-ray diffraction (XRD) using a Bruker D8 DAVINCI diffractometer with Cu-K α radiation, in a 2θ range from 20 to 80° with a step size of 0.01°. Experimental data were analyzed by the Rietveld method using the FullProf program [20].

Chemical compositions were determined by Electron Probe Micro-Analysis (EPMA), using a CAMECA SX-100. Prior to analysis, the samples were polished using 3-μm diamond abrasive paste and ethanol solvent on a woven tape.

Pressure composition isotherms (*PCI*) were measured at 25 °C using the Sieverts' method. All compounds were crushed into a 100 μm-powder, introduced into a gauged sample holder and evacuated under dynamic primary vacuum. Five activation cycles were performed for the Mg-containing samples by successive exposure to 2.5 MPa of hydrogen pressure followed by desorption under dynamic primary vacuum at 150 °C.

3 Results

3.1 Phase determination and structural properties

3.1.1 Gd-based system

Gd_{2-x}La_xNi₇ ($x = 0, 0.6, 1$ and 1.5) were characterized by means of XRD and EPMA. Resulting diffraction patterns are presented in Figure 12. Cell parameters and phase amounts determined from Rietveld refinement (Fig. SI-1) and composition derived from EPMA are gathered in Table 1. Even though the Ni content is slightly lower than expected, the final compositions are very close to the nominal ones. Similar results have been observed for Sm and Y-based systems (see below). The four alloys are all *A₂B₇*-type phases. The binary Gd₂Ni₇ crystallizes in a mixture of *2H* (37%) and *3R* phase (63%). The hexagonal *2H* structure content increases to 54% for Gd_{1.4}La_{0.6}Ni₇ alloy, whereas GdLaNi₇ and Gd_{0.5}La_{1.5}Ni₇ are single phase with *2H* structure (100%). Both cell parameters *a* and *c* increase with La content.

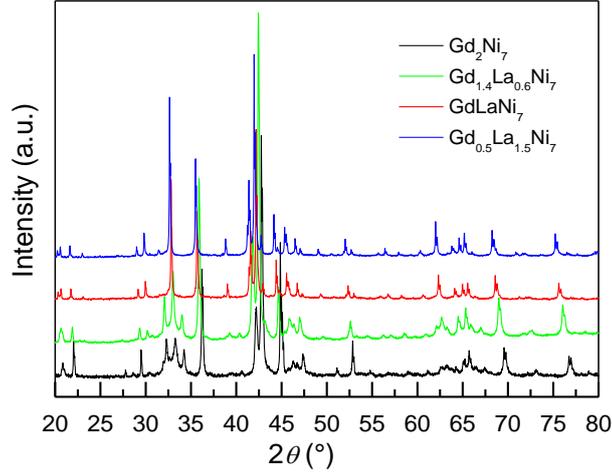


Figure 1: XRD patterns for the $Gd_{2-x}La_xNi_7$ system (from bottom up $x = 0, 0.6, 1, 1.5$).

Table 1: Crystallographic parameters and chemical analysis for the Gd-based system.

Compound	EPMA Composition ± 0.02	<i>Rhombohedral - 3R</i>				<i>Hexagonal - 2H</i>			
		a (Å)	c (Å)	V (Å ³)	Wt.%	a (Å)	c (Å)	V (Å ³)	Wt.%
Gd₂Ni₇	Gd ₂ Ni _{6.93}	4.9608(4)	36.357(5)	774.86(7)	63(3)	4.9621(8)	24.230(3)	516.67 (6)	37(3)
Gd_{1.4}La_{0.6}Ni₇	Gd _{1.4} La _{0.6} Ni _{6.97}	5.0006(4)	36.504(4)	790.5(1)	46(3)	5.0015(4)	24.343(3)	527.4(1)	54(3)
GdLaNi₇	Gd _{0.99} La _{1.01} Ni _{6.91}					5.0225(2)	24.423(1)	533.55(4)	100
Gd_{0.5}La_{1.5}Ni₇	Gd _{0.48} La _{1.52} Ni _{6.90}					5.0446(1)	24.558(1)	541.23(2)	100

3.1.2 Sm-based system

Figure 13 shows the XRD patterns for $Sm_{2-x}La_xNi_7$ ($x = 0, 0.5, 1, 1.5$). Phase percentages and cell parameters derived from Rietveld refinement (Fig. SI-2) are summarized in Table 2, as well as EPMA results. As with the Gd, the samples are A_2B_7 -type phases crystallizing in the two polymorphs $2H$ and $3R$. The relative amount of each polymorphic structure does not show clear dependence with the La content. Diffraction peaks in the angular range 30° - 35° overlapped, which is typical of stacking faults in A_2B_7 compounds. Therefore, the amount of rhombohedral structure determined by Rietveld analysis is slightly over-estimated, especially for $x = 1.5$, where the two peaks (1 0 10) and (0 1 11) are heavily overlapped and hardly noticeable. Lattice parameters increase with La content for both hexagonal and rhombohedral structures.

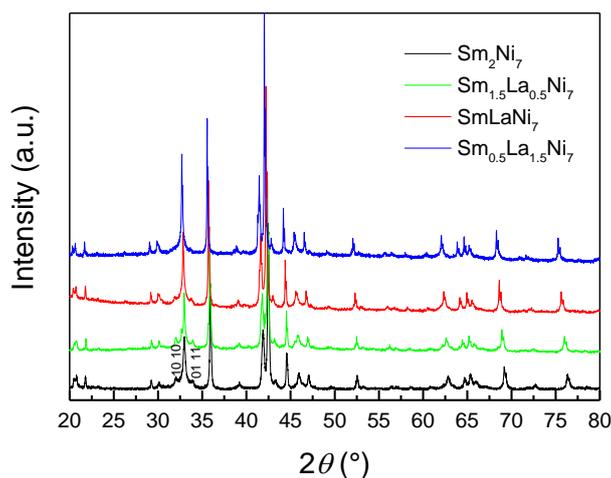


Figure 2: XRD patterns for the system $\text{Sm}_{2-x}\text{La}_x\text{Ni}_7$ (from bottom up $x=0, 0.5, 1, 1.5$). The two hkl peaks (1 0 10) and (0 1 11) heavily overlapped between $30\text{-}35^\circ$ are shown for $x=0$.

Table 2: Crystallographic parameters and chemical analysis for the Sm-based system.

Compound	EPMA Composition ± 0.02	Rhombohedral - 3R				Hexagonal - 2H			
		a (Å)	c (Å)	V (Å ³)	Wt.%	a (Å)	c (Å)	V (Å ³)	Wt.%
Sm₂Ni₇	Sm ₂ Ni _{6.91}	4.9801(2)	36.487(2)	783.70(6)	24(3)	4.9800(2)	24.3290(1)	522.51(5)	76(3)
Sm_{1.5}La_{0.5}Ni₇	Sm _{1.52} La _{0.48} Ni _{6.96}	5.0112(1)	36.59(1)	795.7(2)	37(3)	5.0052(3)	24.393(2)	529.23(6)	63(3)
SmLaNi₇	Sm _{0.97} La _{1.03} Ni _{6.93}	5.0246(1)	36.696(1)	802.33(1)	21(3)	5.0249(2)	24.464(2)	534.94(5)	79(3)
Sm_{0.5}La_{1.5}Ni₇	Sm _{0.51} La _{1.41} Ni _{6.87}	5.0457(1)	36.865(1)	812.83(5)	15(3)	5.0451(1)	24.573(1)	541.74 (3)	85(3)

3.1.3 Y-based system

A selection of four XRD patterns ($x = 0, 0.6, 1$ and 1.5) are shown in Figure 14 for the $\text{Y}_{2-x}\text{La}_x\text{Ni}_7$ system (all XRD patterns for $x = 0, 0.4, 0.5, 0.6, 0.8, 1, 1.5, 1.75$ and 2 are given in Fig. SI-3). Table 3 gives the results from Rietveld refinements (Fig. SI-4) and EPMA analysis. Y_2Ni_7 crystallizes in pure Gd_2Co_7 -type phase. Up to $x = 0.8$, $\text{Y}_{2-x}\text{La}_x\text{Ni}_7$ crystallize in a mixture of 3R and 2H phases. For higher La content ($x = 1, 1.5, 1.75, 2$), the compounds crystallize in pure 2H structure. As with the Gd- and Sm-systems, cell parameters (and cell volume) increase with the La content whatever the structures 3R and 2H.

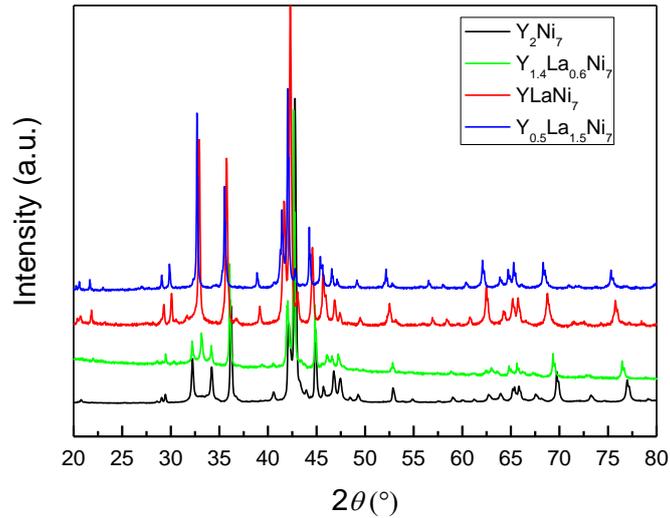


Figure 3: XRD patterns for the system $Y_{2-x}La_xNi_7$ (from bottom up $x = 0, 0.6, 1, 1.5$).

Table 3: Crystallographic parameters and chemical analysis for the Y-based system.

Compound	EPMA Composition ± 0.02	<i>Rhombohedral - 3R</i>				<i>Hexagonal - 2H</i>			
		a (Å)	c (Å)	V (Å ³)	Wt.%	a (Å)	c (Å)	V (Å ³)	Wt.%
Y₂Ni₇	Y ₂ Ni _{6.92}	4.9465(3)	36.260(2)	768.19(7)	100				
Y_{1.6}La_{0.4}Ni₇	Y _{1.59} La _{0.41} Ni _{6.83}	4.9800(1)	36.335(1)	781.06(3)	51(3)	4.9805(2)	24.244(2)	520.81(5)	49(3)
Y_{1.5}La_{0.5}Ni₇	Y _{1.49} La _{0.51} Ni _{6.82}	4.9880(2)	36.399(2)	784.26(7)	56(3)	4.9904(5)	24.275(4)	523.6(1)	44(3)
Y_{1.4}La_{0.6}Ni₇	Y _{1.39} La _{0.61} Ni _{6.91}	4.9929(2)	36.412(2)	786.11(7)	74(3)	4.9935(5)	24.272(3)	524.1(1)	26(3)
Y_{1.2}La_{0.8}Ni₇	Y _{1.18} La _{0.82} Ni _{7.01}	5.0072(1)	36.488(1)	792.27(1)	55(3)	5.0062(1)	24.317(1)	527.18(1)	45(3)
YLaNi₇	Y _{1.01} La _{0.99} Ni _{6.86}					5.0162(3)	24.3601(2)	530.82(6)	100
Y_{0.5}La_{1.5}Ni₇	Y _{0.45} La _{1.55} Ni _{6.94}					5.0405(2)	24.509(1)	539.27(4)	100
Y_{0.25}La_{1.75}Ni₇	Y _{0.23} La _{1.77} Ni _{6.80}					5.0540(1)	24.630(1)	544.83(1)	100
La₂Ni₇	La ₂ Ni _{6.86}					5.0627(4)	24.714(1)	548.57(2)	100

3.1.4 Mg-substituted compounds

The XRD patterns for the $A_{0.5}La_{1.1}Mg_{0.4}Ni_7$ system ($A = Gd, Sm$ and Y) are shown in Figure 15. Structural analysis are summarized in Table 4 and Rietveld refinements are shown in Fig. SI-5. For sake of comparison, crystal data for $La_{1.5}Mg_{0.5}Ni_7$ are also listed from literature [11]. For all compounds, both polymorphs are observed for these quaternary systems and their cell parameters decrease following the order $Sm > Gd > Y$.

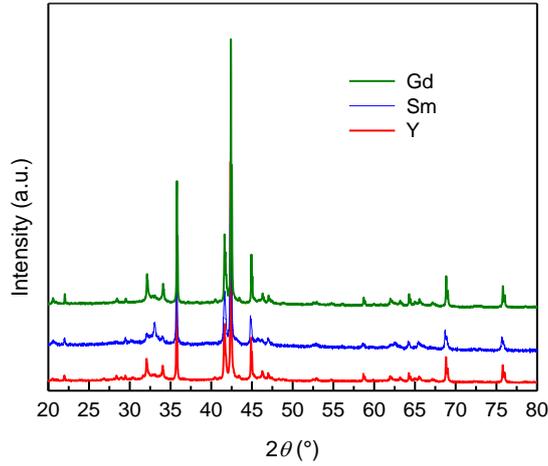


Figure 4: XRD patterns for the $A_{0.5}La_{1.1}Mg_{0.4}Ni_7$ compounds (from bottom up $A = Y, Sm$ and Gd).

Table 4: Crystallographic parameters for the $A_{0.5}La_{1.1}Mg_{0.4}Ni_7$ system ($A = Gd, Sm$ and Y) derived from Rietveld refinements in comparison with $La_{1.5}Mg_{0.5}Ni_7$ obtained from the literature[11]

Compound	<i>Rhombohedral - 3R</i>				<i>Hexagonal - 2H</i>			
	a (Å)	c (Å)	V (Å ³)	Wt.%	a (Å)	c (Å)	V (Å ³)	Wt.%
$La_{1.5}Mg_{0.5}Ni_7$ [11]	5.035	36.309	797.13	57	5.034	24.200	531.00	43
$La_{1.1}Gd_{0.5}Mg_{0.4}Ni_7$	5.0145(1)	36.285(2)	790.16(1)	74(3)	5.0148(1)	24.193(2)	526.89(1)	26(3)
$La_{1.1}Sm_{0.5}Mg_{0.4}Ni_7$	5.0213(4)	36.350 (3)	793.7(1)	42(3)	5.0227(3)	24.252(2)	529.85(6)	58(3)
$La_{1.1}Y_{0.5}Mg_{0.4}Ni_7$	5.0126(2)	36.276 (2)	789.37(6)	76(3)	5.0130(2)	24.182(1)	526.30(4)	24(3)

3.2 Thermodynamic properties

3.2.1 Gd-based system

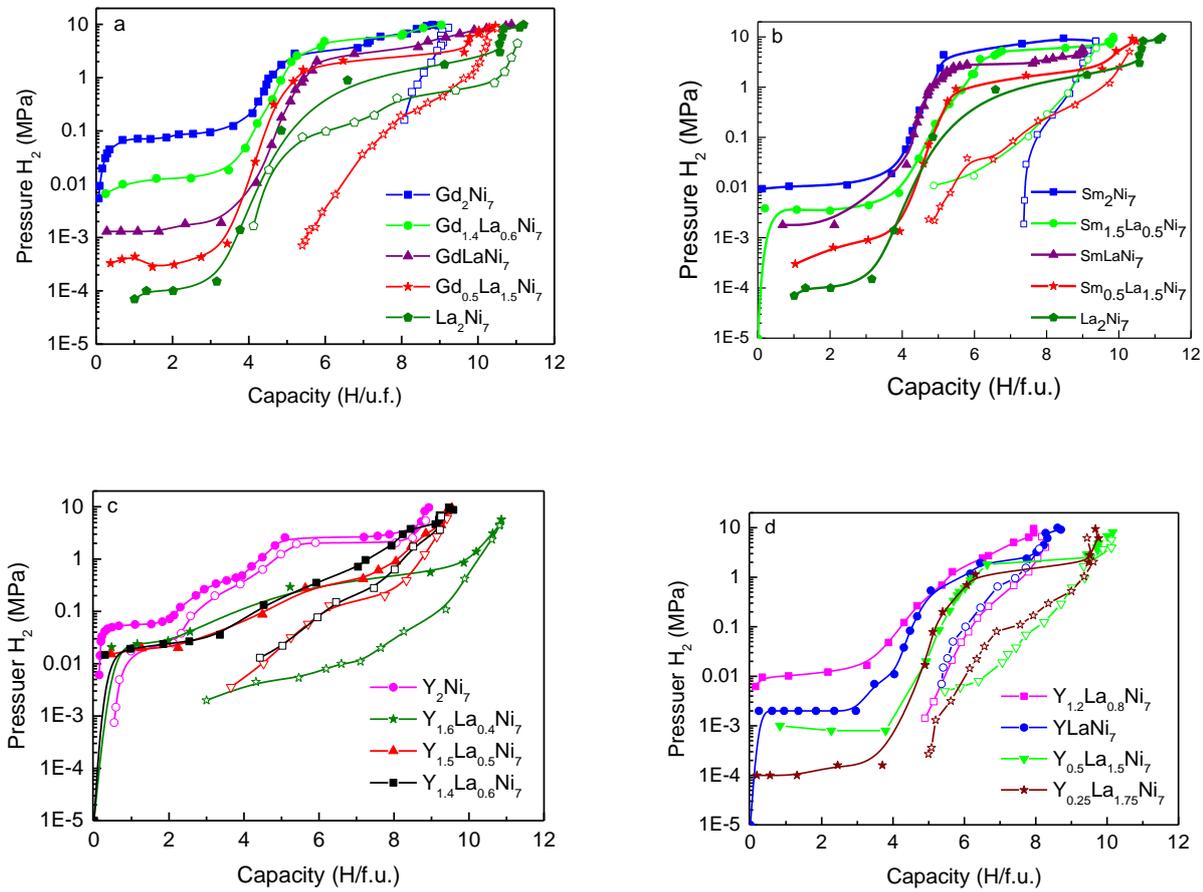
P - c isotherms were recorded for the $Gd_{2-x}La_xNi_7$ system ($0 \leq x \leq 1.5$) and are shown in Figure 5 (a). For sake of clarity, all desorption curves are not shown though they were all measured. All compounds exhibit two absorption plateaus and the first plateaus show almost the same hydrogen range between 0.5 and 3.5 H/f.u.. The plateau pressure decreases with La content from 0.08 MPa for Gd_2Ni_7 to $3 \cdot 10^{-4}$ MPa for $Gd_{0.5}La_{1.5}Ni_7$. As for the second plateau, the hydrogen absorption capacity is nearly constant as well. With La content increasing up to $x=1.5$, the PCI shows the same shape as La_2Ni_7 with a second plateau at higher pressure 2.2 MPa and a smaller hydrogen content between 5.4 and 9.7 H/f.u.. The hydrogen desorption ranges are between those of Gd_2Ni_7 (almost no reversibility) and La_2Ni_7 for which the second plateau is partially reversible.

3.2.2 Sm-based system

PCI for the $Sm_{2-x}La_xNi_7$ system ($0 \leq x \leq 1.5$) are plotted in Figure 5 (b). Like Gd-based compounds, two absorption plateaus are observed. The maximum capacity of the first plateau is 3.5 H/f.u. and does not change significantly with the La content while the plateau pressure decreases significantly from 0.01 MPa for Sm_2Ni_7 to $4.6 \cdot 10^{-4}$ MPa for $Sm_{0.5}La_{1.5}Ni_7$. For the upper (2nd) plateau, the capacity increases with xLa except for $SmLaNi_7$, which shows the lowest capacity. The second absorption plateau pressure decreases slowly with La. For hydrogen desorption, the La substitution improves the desorption ability though it remains incomplete for all compounds.

3.2.3 Y-based system

PCI for $Y_{2-x}La_xNi_7$ system ($0 \leq x \leq 2$) are presented in Figure 5 (c) and (d). Y_2Ni_7 exhibits three plateaus. The first one at 0.055 MPa which covers a range between 0.4 and 2 H/f.u.; the second plateau is located at 0.5 MPa between 3.1 and 4 H/f.u. and the final plateau at 2.9 MPa between 5 and 8.4 H/f.u. For $0.4 \leq x \leq 0.6$, we observe a plateau at 0.02 MPa up to 3.5 H/f.u., followed by a sloppy branch. While a slight decrease of the first plateau is observed, the second and third ones go down drastically making the PCI curves like a sloppy branch. The compound with $x = 0.4$ exhibits a large capacity of 10.9 H/f.u., and the three compounds show good reversibility. The incomplete desorption are mainly due to the Sieverts' apparatus (small H_2 aliquots at very low pressure and limited desorption volume). For $x \geq 0.8$, PCI curves show two plateaus (like for La_2Ni_7) but at higher pressures. $Y_{1.2}La_{0.8}Ni_7$ and $YLaNi_7$ show shorter second plateaus, up to 10 MPa, the upper limit of our measurement range, with capacity of 8 and 8.7 H/f.u., respectively. For $x=1.5$ and 1.75, the pressure of the second plateau is clearly reduced and the maximum capacity increases to 10.2 H/f.u.. For the desorption, only one part of the second plateau is observed.



c

Figure 5: PCI for the system $A_{2-x}La_xNi_7$ with $A = Gd$ (a), Sm (b) or Y (c,d) measured at 25°C, full symbol stand for absorption, open symbols stand for desorption.

3.2.4 Mg-substituted compounds

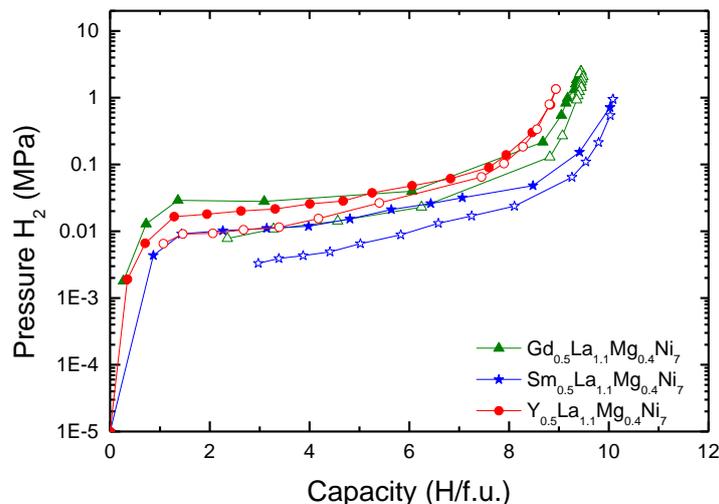


Figure 6: *PCI* for the system $A_{0.5}La_{1.1}Mg_{0.4}Ni_7$ ($A = Sm, Gd$ or Y) measured at $25^\circ C$, full symbols for absorption, open symbols for desorption.

PCI curves measured at $25^\circ C$ for $A_{0.5}La_{1.1}Mg_{0.5}Ni_7$ ($A = Sm, Gd$ or Y) are presented in Figure 17. Outstandingly, all Mg-substituted compounds exhibit only one flat single plateau, with large capacity up to 9~10 H/f.u., in the pressure range between 0.01 and 0.1 MPa and exhibit excellent reversibility.

4 Discussion

4.1 Structural properties of the pseudo-binary systems $A_{2-x}La_xNi_7$

As expected, the A element (Gd, Sm and Y) can be substituted by La in the whole range for A_2B_7 phases, although the abundance of each polymorph changes with composition (see below). On the contrary, for Mg substitution, magnesium can only occupy half of the A sites in the $[A_2B_4]$ subunits, so the maximum Mg content equals to 0.5 for $A_{2-x}Mg_xNi_7$ [18].

EPMA analysis show a slight sub-stoichiometry for Ni in all pseudo-binary A -La-Ni systems. Similar results have already been reported in the La(Nd)-Mg-Ni system [21–23], and explained by the presence of possible Ni vacancies or anti-site occupations of Ni by Mg. In the present pseudo-binary systems, it is very unlikely to occupy Ni sites by rare earths (Sm, Gd or Y). Therefore, the presence of some Ni vacancies is hypothesized.

All A_2Ni_7 pseudo-binary alloys herein studied adopt either the Ce_2Ni_7 -type $2H$ or the Gd_2Co_7 -type $3R$ structure. The two structures differ only in the basic periods stacked along the c axis. As a general rule, the larger A atoms favor the formation of the $2H$ structure[24], but the thermal and synthesis history influence also sensibly the formation of either the $2H$ or $3R$ structure[25]. Although the synthesis process slightly differs depending on the composition. Figure 7 shows that for the A_2Ni_7 binary compounds ($A = Y, Gd, Sm$ or La), the ratio of hexagonal/rhombohedral structure increases with r_A , same effect has been reported in the $(NdA)_{1.5}Mg_{0.5}Ni_7$ ($A=La, Y$) system[26] as well as

(La,Y)₂Ni₇ system [26,27]. As for the pseudo-binary compounds, the content of hexagonal phase increases with *x*La. For *A* = Y or Gd, when *x* ≥ 1, the compounds are single phase with hexagonal structure. Surprisingly, for *A* = Sm, which is larger than Y and Gd, the critical value is higher than *x* = 1.5.

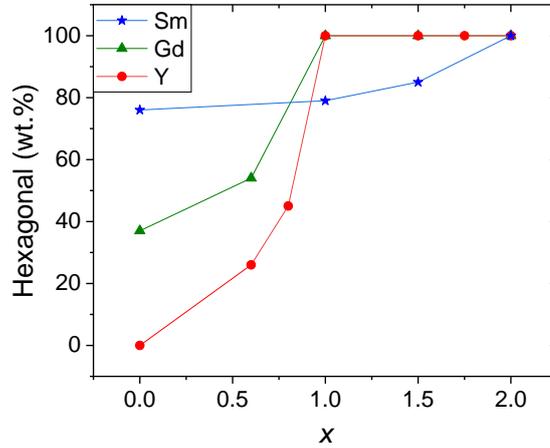


Figure 7: Evolution of the percentage of hexagonal phase in the $A_{2-x}La_xNi_7$ systems. The outliers (for $x = 0.4$ and 0.5) were removed.

For sake of comparison between the hexagonal and rhombohedral structures, the *c* parameter and the cell volume *V* have been divided by 6 and 9 for $2H$ and $3R$, respectively, to compare the average parameter c^* and volume V^* . Evolutions of the parameters *a*, c^* , V^* , and c^*/a ratio *versus* *x*La are reported in Figure 19 for the pseudo-binary systems $A_{2-x}La_xNi_7$. The cell parameters *a* (a_H and a_R) and c^* increase continuously with La content following a second order polynomial law with opposite curvatures. Besides, a linear increase of the reduced cell volume V^* is observed with *x*La for the three elements *A*. Despite the non-linear behavior of the cell parameters, the opposite effects compensate each other, and the average subunit volume increases linearly with *x*La as expected for a solid solution, following the Vegard's law[28]. The slope factor is logically related to the atomic radius difference between La and the different *A* atoms following the sequence $\Delta R_{Y-La} > \Delta R_{Gd-La} > \Delta R_{Sm-La}$.

For all $A_{2-x}La_xNi_7$ alloys, the c^*/a ratio shows a power law with first a decrease with increasing La content, reaching a minimum for $x = 1$ and then an increase up to $x = 2$. This behavior is tightly related to the site occupation of partially substituted La atoms. Refinement of the rare-earth occupancy factors show that at lower *x*, La occupies preferentially the sites $4f_2^H$ ($6c_1^R$) belonging to the $[ANi_5]$ subunits. This can be understood based on a geometric effect: La is larger than Y, Sm or Gd, thus it fills the $4f_2^H$ ($6c_1^R$) sites with higher coordination number than the $4f_1^H$ ($6c_2^R$) ones (20 *versus* 16). This result has been confirmed by DFT calculation for the system $La_{2-x}Y_xNi_7$, where it was shown that the enthalpies of formation are lower with Y occupying the $[A_2Ni_4]$ subunit sites and La the $[ANi_5]$ subunit one[27]. Replacing Y by La in the $[ANi_5]$ slabs leads to an expansion of this slab parallel to the *ab* plan[15,29]. By epitaxy, this also induces the stretching of the $[A_2Ni_4]$ in the *ab* plan, but no effect along the *c* axis since no substitution arises in this slab. Such anisotropic behavior leads then to a larger cell parameter increase for *a* than for *c*. This behavior is observed up to the composition $LaANi_7$ ($x=1$), for which La replaced all *A* atoms in $[ANi_5]$. The stacking structure can then be written as $2 \cdot [LaNi_5] + [A_2Ni_4]$. Above this composition, La starts to substitute the *A* sites within the $[A_2Ni_4]$ slab. The cell parameter *a* increases slightly, because it has already been expanded within the $[ANi_5]$ slab,

whereas c increases rapidly due to the volume expansion of the $[A_2Ni_4]$ slab by La substitution. These hypotheses are confirmed by the evolution of the c^*/a ratio (Figure 19c) that shows a quicker expansion of a vs c^* for $0 < x < 1$ and *vice-versa* for $1 < x < 2$.

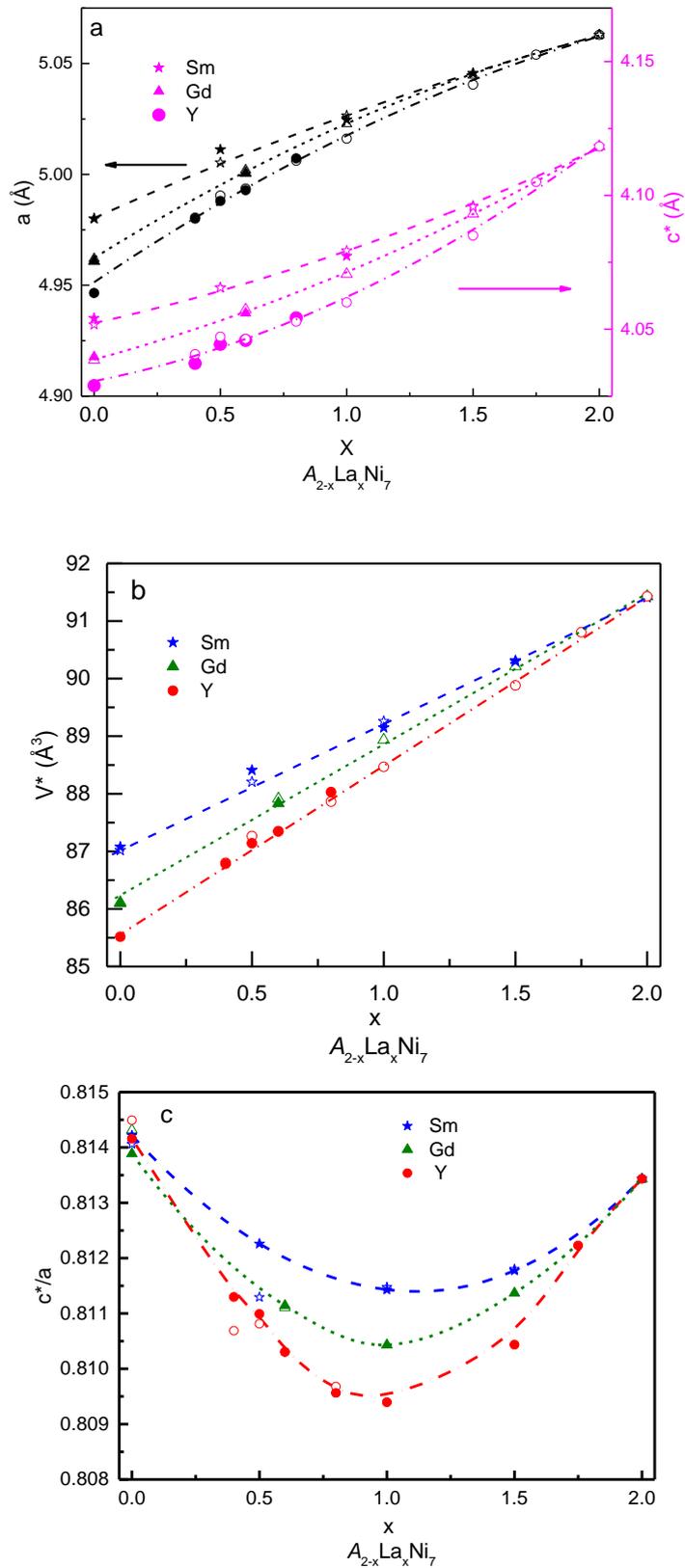


Figure 8 : Evolution of cell parameters a and c^* (a), cell volume V^* (b) and c^*/a ratio versus xLa content for the pseudo-binary systems $A_{2-x}La_xNi_7$, full symbols for hexagonal structure, open symbols for rhombohedral structure

4.2 Hydrogenation properties of the pseudo-binary systems $A_{2-x}La_xNi_7$

4.2.1 Comparison of A_2Ni_7 binary compounds

PCI for the binary compounds A_2Ni_7 ($A = Y, Gd, Sm$ or La) are compared in Figure 9. All compounds show two plateaus except Y_2Ni_7 with three plateaus. A previous neutron diffraction analysis of $Y_2Ni_7D_z$ has shown that up to the end of the second plateau (i.e. $Y_2Ni_7D_4$), hydrogen fills mainly the available sites in the $[Y_2Ni_4]$ subunit, whereas the third plateau corresponds to the filling of the $[YNi_5]$ one [30]. Anisotropic cell volume expansion has already been observed upon hydrogenation for several AB_y compounds ($2 < y < 5$) such as $La_2Ni_7D_{6.5}$ [31], $CeNi_3D_{2.8}$ [12,32], $Ce_2Ni_7D_{4.7}$ [33], $LaNi_3D_{2.8}$ [34], $CeY_2Ni_9D_{7.7}$ [35] and $Y_2Ni_7D_{2.1}$ [30]. Anisotropic expansion is due to the fact that hydrogen (deuterium) first occupies the $[A_2B_4]$ subunits, for which the ab plane is constrained by the surrounding and non-hydrogenated $[AB_5]$ subunits. As those studies pointed out, the individual volume of $[A_2B_4]$ is larger than that of $[AB_5]$, moreover the $[A_2B_4]$ subunits contain 2 A -elements instead of one for $[AB_5]$. Thus, $[A_2B_4]$ subunits are richer in A and thus more favorable for hydrogen hosting than $[AB_5]$ ones. These differences in geometry and chemistry are the main factors for the multi-plateau behavior of these stacking-structure compounds. Reasonably, we can presume that for binary systems like Gd_2Ni_7 , Sm_2Ni_7 and La_2Ni_7 , the first plateau corresponds to $[A_2Ni_4]$ -H filling whereas the second one is consistent with the filling of $[ANi_5]$.

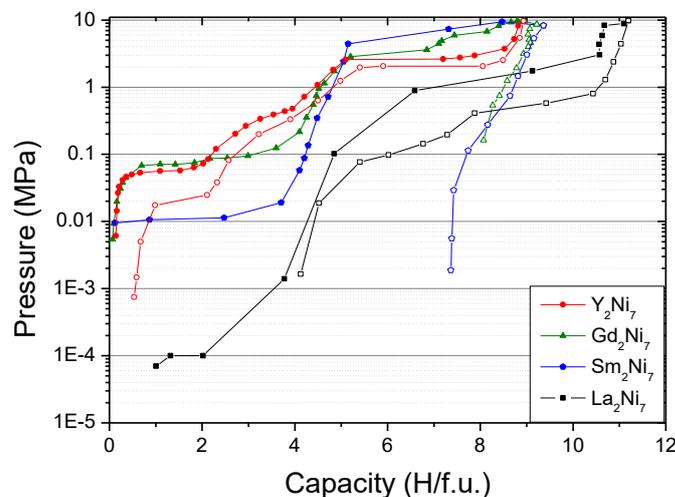


Figure 9: PCI curves for La_2Ni_7 , Sm_2Ni_7 , Gd_2Ni_7 and Y_2Ni_7 measured at $25^\circ C$ by the Sieverts' method. Filled and hollow symbols correspond to absorption and desorption curves respectively.

Focusing on the first plateau, the equilibrium pressure increases, while the A atomic size decreases. La_2Ni_7 shows a lower plateau than Sm_2Ni_7 , which is lower than that of Gd_2Ni_7 . Indeed, as the rare earths have very similar chemical properties, the $A_2Ni_7H_{\sim 4}$ hydride stability is dominated by geometric parameters. A smaller atom size leads to a smaller cell volume, needing higher energy and consequently higher hydrogen pressure for hydrogenation. However, the first plateau of Y_2Ni_7 is

slightly below that of Gd_2Ni_7 , although Y being smaller than Gd. This can be originated by the higher affinity of yttrium for hydrogen, as the formation enthalpy of YH_3 is slightly higher than that of GdH_3 [36]. Another reason might be related to the difference in electronic configuration due to the 4f-electrons of lanthanides compared to f-electron free yttrium.

For the second plateau, La_2Ni_7 provides the lowest plateau pressure and the highest capacity, while Sm_2Ni_7 , Gd_2Ni_7 and Y_2Ni_7 exhibit lower capacities and higher plateau pressures than La_2Ni_7 . Thus, the hydrogenation properties of those compounds cannot be described by a simple linear combination of the ones of their AB_2 and AB_5 counterparts. However, assuming that the second plateau corresponds to the filling of the $[\text{ANi}_5]$ subunits only, one can expect some relationship between the thermodynamic properties of the second plateau of the $A_2\text{Ni}_7$ and ANi_5 compounds. Lanthanum is well-known as a good candidate to form hydride in the ANi_5 system. At room temperature, LaNi_5 shows one flat plateau at 0.17 MPa with a capacity of 6.6 H/f.u. and a very small hysteresis [37]. GdNi_5 and SmNi_5 show two plateaus, the first one with a capacity of 4 H/f.u. followed by a second one of 2H/f.u. at much higher pressure (above 20 MPa at 25°C) [38,39]. Moreover, the hysteresis between absorption and desorption is quite high for these two compounds. These differences between LaNi_5 and both GdNi_5 and SmNi_5 can explain the large capacity and lower plateau pressure of La_2Ni_7 compared to the smaller capacities and higher plateau pressures of Gd_2Ni_7 and Sm_2Ni_7 .

The *PCI* of Gd_2Ni_7 and La_2Ni_7 have been previously reported [16,40]. For La_2Ni_7 , our results are in good agreement with the literature. La_2Ni_7 transforms from hexagonal to orthorhombic then to monoclinic structure, corresponding to the filling of hydrogen in $[\text{La}_2\text{Ni}_4]$ and $[\text{LaNi}_5]$ subunits, respectively. While the first transformation is irreversible (hydrogen is trapped in $[\text{La}_2\text{Ni}_4]$ subunits), the second plateau, where hydrogen fills $[\text{LaNi}_5]$ subunits, can absorb and desorb hydrogen reversibly. For Gd_2Ni_7 , a total reversibility at low temperature (258 K) was reported for a sample with a quasi-single hexagonal structure [40]. In our work, we attempted to measure the *PCI* desorption at lower temperature without success due to the sluggish kinetics. As for Sm_2Ni_7 , it behaves similarly to Gd_2Ni_7 showing poor reversibility.

Y_2Ni_7 exhibits excellent hydrogen uptake/release reversibility, which is an exception among all $A_2\text{Ni}_7$ binary compounds ($A = \text{Y}$ or lanthanide). Fang *et al.* [41] found that the dehydrogenation properties of AB_3 compounds are closely related to their subunit volume. They found that whatever the composition, a $[\text{AB}_5]$ subunit volume below 88.3 \AA^3 and a $[\text{A}_2\text{B}_4]$ one below 89.2 \AA^3 are the prerequisite conditions for the reversible hydrogen desorption. For Y_2Ni_7 , the $[\text{A}_2\text{B}_4]$ and $[\text{AB}_5]$ volumes are 86.1 and 85.1 \AA^3 respectively, fulfilling the prerequisite conditions for hydrogen desorption according to Fang *et al.* A_2B_7 are compounds with stacking structure, differing from AB_3 only by the number of $[\text{AB}_5]$ subunits (2 instead 1 for AB_3). Their criterion could thus be valid for A_2B_7 system too. However, Y_2Ni_7 is not the only compound fulfilling these conditions. Gd_2Ni_7 exhibits similar crystallographic geometry with $[\text{A}_2\text{B}_4]$ and $[\text{AB}_5]$ volumes of 86.1 and 86.1 \AA^3 , respectively (Figure 11). Under our experimental conditions, reversibility for Gd_2Ni_7 was not observed, it might be related to kinetic issues rather than thermodynamic ones.

4.2.2 Effect of the substitution of Sm, Gd or Y by La

Substitution of A by lanthanum leads to a decrease of the first plateau pressure. Since La is larger than Gd, Sm and Y, the substitution increases the cell volume and consequently decreases the plateau pressure. As pointed out by Mendelsohn *et al.*, $\ln(P_{\text{eq}})$ is directly proportional to the inverse of the cell volume (with P_{eq} the equilibrium plateau pressure) [42]. Equilibrium pressures measured for the first plateau, attributed to the filling of the $[\text{A}_2\text{Ni}_4]$ subunit, are plotted against the average subunit cell volumes in Figure 21. The $\ln(P_{\text{eq}})$ shows a very good linear correlation with the average subunit

volume V^* . It confirms that the geometrical rule is also valid for the first plateau of those compounds with multi-plateau behavior.

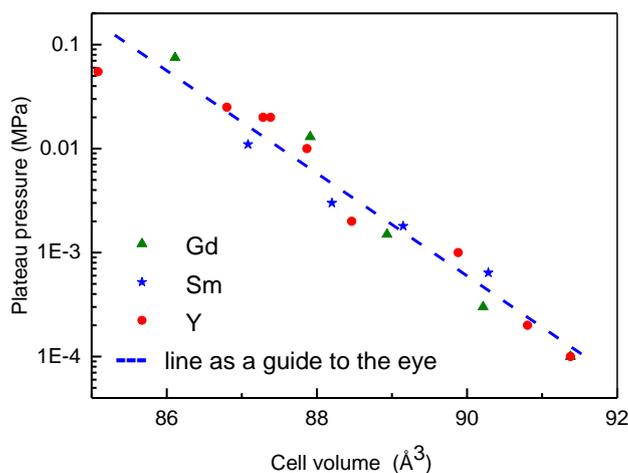


Figure 10: $\text{Ln}(P_{\text{eq}})$ measured for the first plateau as a function of the average subunit volume V^* for $A_{2-x}\text{La}_x\text{Ni}_7$ ($A = \text{Gd}, \text{Sm}, \text{Y}$).

For the second plateau, the behavior needs more detailed inspection. Surprisingly, for Gd_2Ni_7 (Figure 5. a), substitution of Gd by La does not affect significantly the second plateau up to the composition GdLaNi_7 , which corresponds to the stacking scheme $2 \cdot [\text{LaNi}_5] + [\text{Gd}_2\text{Ni}_4]$, *i.e.* substitution in $[\text{AB}_5]$ unit only. Further increase in La content ($\text{Gd}_{0.5}\text{La}_{1.5}\text{Ni}_7$) leads to a plateau stabilization between those of La_2Ni_7 and Gd_2Ni_7 . In the case of Sm_2Ni_7 (Figure 5.b), substitution of Sm by La causes a continuous decrease of the plateau pressure with x .

Finally, for Y_2Ni_7 , La substitution for Y leads to more complex behavior for the second plateau pressure. Low La substitution for Y results in a drastic diminution of the plateau pressure and an augmentation of the capacity. To understand this, the subunit volumes of $[\text{A}_2\text{B}_4]$ and $[\text{AB}_5]$ are plotted in Fig. SI-6 for the $\text{Y}_{2-x}\text{La}_x\text{Ni}_7$ compounds as a function of $x\text{La}$. First, when Y is substituted by small amount of La, the $[\text{AB}_5]$ volume increases rather sharply, which can be explained by the fact that La occupies preferentially the A site in $[\text{ANi}_5]$ subunit, leading to an expansion of the ab plane. Thus, it induces an increase of the $[\text{A}_2\text{B}_4]$ subunit volume, and therefore explain the diminution of the plateau pressure and capacity increase. Up to $x = 0.8$, the subunit volumes of $[\text{A}_2\text{B}_4]$ and $[\text{AB}_5]$ are still smaller than the reported critical volume (figure 10), which may be the reason for the sloppy PCI curve and the better reversibility. For $x > 1$, La starts to occupy the $[\text{A}_2\text{B}_4]$ units, the compounds behave like La_2Ni_7 . The difference between the volumes of $[\text{A}_2\text{B}_4]$ and $[\text{AB}_5]$ increases sharply and stands out of the critical limit for reversibility. Those compounds have smaller cell volumes, thus higher plateau pressures compared to La_2Ni_7 , but similar poor reversibility (Figure 10). However, for fundamental understanding, neutron diffraction of those compounds at different hydrogen contents should be interesting to localize H atoms in the structure.

4.2.3 Effect of the substitution of Sm, Gd or Y by La and Mg

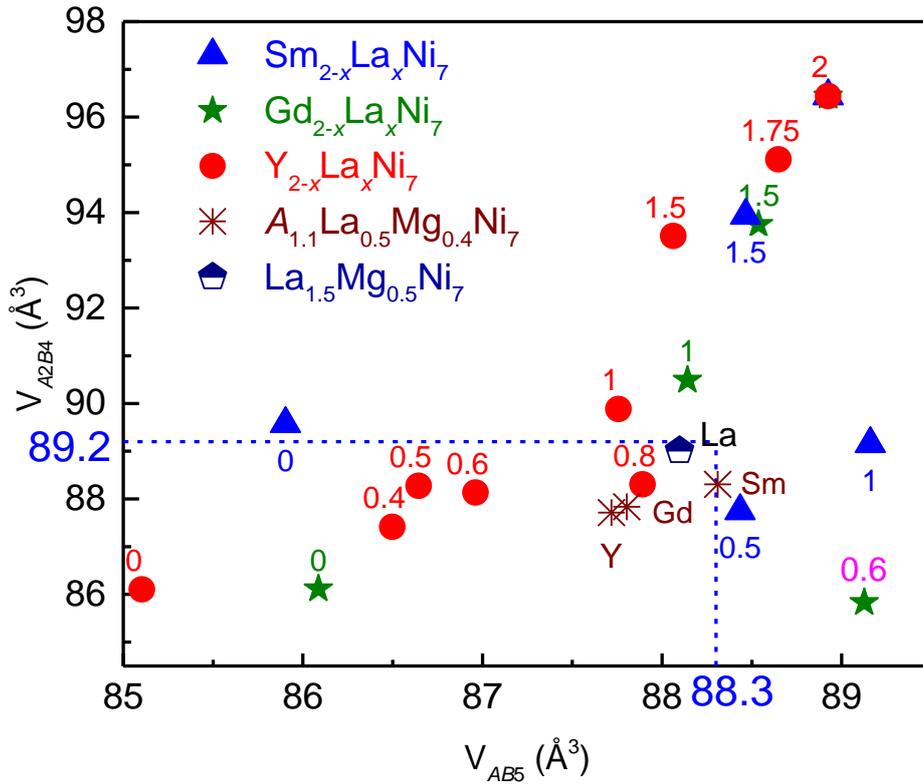


Figure 11: The $[AB_5]$ and $[A_2B_4]$ subunit volumes for the studied compounds together with the “reversibility limits” giving by Fang *et al.* [41].

PCI of $\text{La}_{1.1}\text{A}_{0.5}\text{Mg}_{0.4}\text{Ni}_7$ ($A = \text{Sm}, \text{Gd}$ or Y) are compared in Figure 17. All Mg-substituted compounds show flat plateaus with good reversibility and low hysteresis. As mentioned before, the mismatch between the $[AB_5]$ and $[A_2B_4]$ subunits and the too large ratio r_A/r_B are the main causes for the HIA and irreversibility for stacked structure compounds[19,34,43–45]. These authors state that HIA can be suppressed by reducing the subunit volume difference below 5.3 \AA^3 [46,47]. Recently, Fang *et al.* pointed out that this criterion is not enough for hydrogen release. They claim that the subunits $[AB_5]$ and $[A_2B_4]$ should not be larger than 88.3 and 89.2 \AA^3 , respectively. Table 5 summarizes the average subunit and cell volumes of $[AB_5]$ and $[A_2B_4]$ for the Mg substituted compounds studied in this work and $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$, one of the most studied composition with promising hydrogen storage properties[11]. One can see that all these compounds exhibit $[AB_5]$ and $[A_2B_4]$ subunit volumes very close to each other and fulfill the critical values of 88.3 and 89.2 \AA^3 respectively (Figure 11), which well explains their outstanding hydrogenation properties. From the point of view of application, these compounds can sorb reversibly large amount of hydrogen at appropriate pressure, ideally flat plateaus in the pressure range 10^{-3} to 0.1 MPa .

Table 5: Subunits ($[AB_5]$ and $[A_2B_4]$) volumes, average subunit volume V^* and c^*/a ratio for the Mg-substituted compounds, compared to the values for $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ [11].

Compounds	V_{AB_5} (\AA^3)	$V_{A_2B_4}$ (\AA^3)	V^* (\AA^3)	c^*/a	Ref.
$\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$	88.09	89.01	88.40	0.804	Zhang [11]
$\text{La}_{1.1}\text{Sm}_{0.4}\text{Mg}_{0.4}\text{Ni}_7$	88.31	88.30	88.31(2)	0.804	this work
$\text{La}_{1.1}\text{Gd}_{0.4}\text{Mg}_{0.4}\text{Ni}_7$	88.20	87.84	87.81(1)	0.804	this work
$\text{La}_{1.1}\text{Y}_{0.4}\text{Mg}_{0.4}\text{Ni}_7$	87.72	87.71	87.71(2)	0.804	this work

For the $(\text{La},\text{Mg})_2\text{Ni}_7$ system, it was reported that Mg substitutes La atoms in the $[A_2\text{Ni}_4]$ units only, up to half of the La sites thus reaching the composition $[\text{LaMgNi}_4]$ [18,31]. Such effect is generally observed in stacking structures as other authors showed similar behavior with $n = 1, 2, 3$ (*i.e.* AB_3 , A_2B_7 and A_5B_{19}) even with other rare earths [48,49]. The specificity of Mg is therefore not only related to its small size (1.599 \AA) but also its localization, as Mg replaces only rare earth located in the $[A_2B_4]$ units, thus involving a drastic reduction of the $[A_2B_4]$ volume. Consequently, the subunit volumes of $[AB_5]$ and $[A_2B_4]$ become closer. It is worth to note that, i) Mg has a smaller atomic radius than rare earths, ii) hydrogen affinity for Mg is lower than for the lanthanides and yttrium. Therefore, Mg substitution shrinks the $[A_2B_4]$ unit and lowers the H affinity, making $[A_2B_4]$ units less attractive for hydrogen. Altogether, it makes the hydrogen occupancies comparable for $[A_2B_4]$ and $[AB_5]$ subunits leading to larger and flatter PCI curves as observed in Figure 17. It is worth to note that such improvement in the hydrogen sorption properties, combined with the molar mass decrease brought by Mg substitution, leads to materials highly suitable for solid-gas or electrochemical energy storage applications.

The plateau pressures of $\text{Gd}_{0.5}\text{La}_{1.1}\text{Mg}_{0.4}\text{Ni}_7$ and $\text{Y}_{0.5}\text{La}_{1.1}\text{Mg}_{0.4}\text{Ni}_7$ are very close. Indeed, the volumes of their stacking subunits are almost identical (Table 5). The average subunit volume of $\text{La}_{1.1}\text{Sm}_{0.5}\text{Mg}_{0.4}\text{Ni}_7$ is however a bit larger ($V_{\text{sm}}^* = 88.31(3) \text{\AA}^3$), consequently the plateau pressure is significantly lower. From the PCI, limiting the practical capacity in the pressure range 0.001 to 0.1 MPa, these compounds give good electrochemical capacities with 350 mAh/g for Y, 370 mAh/g for Gd and 400 mAh/g for Sm-based compounds. The relative lower capacity for Y is due to the higher plateau pressure. Electrochemical properties for similar alloys have been studied and shown interesting capacity and cycle life [50,51]. Therefore, by further compositional adjustment of this compound, the pressure can be optimized thus leading to very promising properties for practical applications.

5 Conclusions

Several Sm, Gd and Y-based compounds with A_2B_7 polymorphic structures have been successfully synthesized in this work. Their structural properties have been investigated and their thermodynamic properties regarding H sorption have been determined at 25°C. For all A_2B_7 compounds, the maximal capacity of the fully hydrided samples (up to 10 MPa) ranges between 9 and 11 H/f.u. Comparison of the PCI curves raise several points:

- Substitution of A by La leads to a decrease of the first plateau pressure, the larger the A element in $A_2\text{Ni}_7$ compounds, the lower the first plateau pressure.
- Substitution of A by La influences the second plateau pressure and the total capacity but it needs more detailed inspection by neutron diffraction to accurately localize H atoms.
- Substitution of A by La and Mg leads to a single, large, stable and reversible plateau pressure, particularly suitable for applications.
- Reversibility can be predicted based on $[A_2B_4]$ and $[AB_5]$ subunits volumes.

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Figure caption:

Figure 12: XRD patterns for the $Gd_{2-x}La_xNi_7$ system (from bottom up $x = 0, 0.6, 1, 1.5$).

Figure 13: XRD patterns for the system $Sm_{2-x}La_xNi_7$ (from bottom up $x=0, 0.5, 1, 1.5$). The two hkl peaks (1 0 10) and (0 1 11) heavily overlapped between $30-35^\circ$ are shown for $x=0$.

Figure 14: XRD patterns for the system $Y_{2-x}La_xNi_7$ (from bottom up $x = 0, 0.6, 1, 1.5$).

Figure 15: XRD patterns for the $A_{0.5}La_{1.1}Mg_{0.4}Ni_7$ compounds (from bottom up $A = Y, Sm$ and Gd).

Figure 16: PCI for the system $A_{2-x}La_xNi_7$ with $A = Gd$ (a), Sm (b) or Y (c,d) measured at $25^\circ C$, full symbol stand for absorption, open symbols stand for desorption.

Figure 17: *PCI* for the system $A_{0.5}La_{1.1}Mg_{0.4}Ni_7$ ($A = Sm, Gd$ or Y) measured at $25^\circ C$, full symbols for absorption, open symbols for desorption.

Figure 18: Evolution of the percentage of hexagonal phase in the $A_{2-x}La_xNi_7$ systems. The outliers (for $x = 0.4$ and 0.5) were removed.

Figure 19 : Evolution of cell parameters a and c^* (a), cell volume V^* (b) and c^*/a ratio versus xLa content for the pseudo-binary systems $A_{2-x}La_xNi_7$, full symbols for hexagonal structure, open symbols for rhombohedral structure

Figure 20: PCI curves for La_2Ni_7 , Sm_2Ni_7 , Gd_2Ni_7 and Y_2Ni_7 measured at $25^\circ C$ by the Sieverts' method. Filled and hollow symbols correspond to absorption and desorption curves respectively.

Figure 21: $\ln(P_{eq})$ measured for the first plateau as a function of the average subunit volume V^* for $A_{2-x}La_xNi_7$ ($A = Gd, Sm, Y$).

Figure 22: The $[AB_5]$ and $[A_2B_4]$ subunit volumes for the studied compounds together with the "reversibility limits" giving by Fang *et al.* [41].