Structural and chemical analyses of the new ternary La$_5$MgNi$_{24}$ phase synthesized by Spark Plasma Sintering and used as negative electrode material for Ni-MH batteries

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ABSTRACT

In the present work, starting from the nominal composition La$_{0.85}$Mg$_{0.15}$Ni$_{3.8}$, samples have been synthesized by SPS (Spark Plasma Sintering) technique at different temperature from 810 °C to 900 °C. The crystallographic structures as well as the phase compositions have been studied by X-ray diffraction (XRD) and Electron-Probe Micro Analysis (EPMA). A new ternary La$_5$MgNi$_{24}$ phase with stacking structure (space group R-3m) has been identified and its structure determined by XRD analysis. This (1:4) phase forms at higher temperature than the (5:19) and (2:7) ones. In the present work, the phases (2:7); (5:19); (1:4) and (1:5) coexist for all samples. The substitution of La by Mg only occurs in the layer corresponding to the Laves phase for all the stacking structure phases. The substitution rate (La/Mg ratio in the Laves layer) is equal to half and does not change with the SPS temperature treatment. The hydrogen storage capacity and the electrochemical capacity are not too much influenced by the SPS temperature. In contrast, the cycling stability shows better resistance to corrosion for the samples containing larger amount of (5:19) phase.

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1. Introduction

Intermetallic compounds with RM$_m$ (3 ≤ m < 5) (R = rare earth or alkaline earth, M = transition metal and Al) formula and various stacking structures have attracted attention as electrode materials for Ni–MH batteries because of their high electrochemical discharge capacity. In 1997, Kadir et al. [1] reported on the RMg$_3$Ni$_3$ system with PuNi$_3$-type superstructure corresponding to a rhombohedral 1:1 stacking of RM$_3$ and R$_2$M$_4$ units. Since then, lot of works have been reported on RM$_m$ (3 ≤ m < 5) alloys [2–10]. These alloys show high electrochemical discharge capacity (340–410 mAh g$^{-1}$) and relatively good cycle life. All these alloys crystallize in so-called stacking structures, either rhombohedral Gd$_5$Co$_7$-type (2:7R), hexagonal Ce$_2$Ni$_7$-type (2:H7), rhombohedral Ce$_5$Co$_{19}$-type (5:19R), or hexagonal Pr$_5$Co$_{19}$-type (5:19H) structure. These structures can be described as a 2:1 or 3:1 stacking of RM$_3$ and R$_3$M$_4$ units along the c axis for R$_2$M$_7$ and R$_5$M$_{19}$, respectively. Beside these phases, a rhombohedral La$_5$MgM$_{24}$-type phase (1:4R) described as a 4:1 stacking of the same units has been newly reported by Ozaki [7] for the La$_5$(Mg$_{0.75}$Mn$_{0.25}$)$_{24}$ composition. Such stacking structure was indeed predicted earlier by Khan [11] in the R-Co system and this author proposed a mathematical
relationship from which atomic positions and lattice parameters can be calculated.

Due to the elevated vapor pressure of magnesium, the Mg content is very difficult to control in these samples. Recently, Spark Plasma Sintering (SPS) technique has attracted much attention for preparing alloys and intermetallic compounds [12–15]. SPS is mainly characterized by spark plasma created from a pulse of direct current during heat treatment of the powders under mechanical pressure. By this way, compounds can be synthesized in a shorter time, at lower temperature and without volatilization of light elements.

In the present work, we report on the structural and chemical analyses of a rhombohedral La₅MgNi₂₄-type phase newly obtained from the SPS synthesis of the La₀.₈₅Mg₀.₁₅Ni₃.₈ composition. A general rule for the stabilization of the stacking structure phases will be proposed. Influence of the SPS temperature treatment on the phase fraction and hydrogenation properties will be discussed.

2. Experiments

Compounds with La₀.₈₅Mg₀.₁₅Ni₃.₈ composition were prepared by SPS starting from two precursors: Mg₂Ni binary phase and a sample with nominal composition LaNi₅ (\( y = 4.33 \)). The LaNi₅ was obtained by induction melting from the pure elements La and Ni. According to the La–Ni phase diagram and to the \( y \) value, this sample contains a mixture of two intermetallic compounds, namely La₅Ni₂₇ (2H and 3R-type structure) and LaNi₅. Mg₂Ni was prepared by powder metallurgy from Ni and Mg elemental powders. The LaNi₅ and Mg₂Ni powders were ball milled together in a Fritsch Puri- verisette P₄ for 2 h and then the mixture was heat treated by SPS under 50 MPa of mechanical pressure for 1 h at temperature ranging between 810 °C and 900 °C. At these temperatures, the Mg₂Ni phase is liquid (\( T_L = 760 ^\circ \text{C} \)) and some losses of Mg by sublimation occur. To correct this effect, the initial mixture was slightly modified by adding a 50% of excess of Mg₂Ni and by decreasing accordingly the Ni content \( y \) in the LaNi₅ system to preserve the nominal composition La₀.₈₅Mg₀.₁₅Ni₃.₈ (\( y = 4.33 \) was used). All the handlings of the sample have been done in a glove box under Ar atmosphere, except for about 2 min to put the SPS die in the chamber and to evacuate the chamber. The synthesized sample weight is about 1 \( \mu \text{g} \) and without volatilization of light elements.

The prepared samples were mechanically evacuated the chamber. The synthesized sample weight is typically 6 g. The prepared samples were ball milled together in a Fritsch Puri-verisette P₄ for 2 h and then the mixture was heat treated by SPS starting from two precursors: Mg₂Ni binary phase and by decreasing accordingly the Ni content \( y \). The mixture was slightly modified by adding a 50% of excess of Mg₂Ni and by decreasing accordingly the Ni content \( y \) in the LaNi₅ system to preserve the nominal composition La₀.₈₅Mg₀.₁₅Ni₃.₈ (\( y = 4.33 \) was used). All the handlings of the sample have been done in a glove box under Ar atmosphere, except for about 2 min to put the SPS die in the chamber and to evacuate the chamber. The synthesized sample weight is about 1 \( \mu \text{g} \) and without volatilization of light elements.

In the present work, we report on the structural and chemical analyses of a rhombohedral La₅MgNi₂₄-type phase newly obtained from the SPS synthesis of the La₀.₈₅Mg₀.₁₅Ni₃.₈ composition. A general rule for the stabilization of the stacking structure phases will be proposed. Influence of the SPS temperature treatment on the phase fraction and hydrogenation properties will be discussed.

3. Results

Table 1 shows the results from ICP analysis giving the average chemical compositions of the samples. It can be observed that magnesium losses during heat treatment are less than anticipated with few changes in the global composition.

Table 1: Chemical compositions obtained from ICP analyses for different SPS heat treatment temperatures for the La₀.₈₅Mg₀.₁₅Ni₃.₈ composition (standard deviation given between brackets).

<table>
<thead>
<tr>
<th>SPS temperature (°C)</th>
<th>La (wt%)</th>
<th>Mg (wt%)</th>
<th>Ni (wt%)</th>
<th>Sum (wt%)</th>
<th>Observed composition</th>
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<tbody>
<tr>
<td>Starting composition</td>
<td>34.07</td>
<td>1.63</td>
<td>64.30</td>
<td>100</td>
<td>La₀.₇₉Mg₀.₂₅Ni₃.₅5</td>
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<tr>
<td>810</td>
<td>32.68 (0.02)</td>
<td>1.56 (0.01)</td>
<td>62.44 (0.08)</td>
<td>96.68 (0.08)</td>
<td>La₀.₇₉Mg₀.₂₅Ni₃.₅5</td>
</tr>
<tr>
<td>820</td>
<td>33.62 (0.02)</td>
<td>1.60 (0.01)</td>
<td>63.93 (0.10)</td>
<td>99.15 (0.10)</td>
<td>La₀.₇₉Mg₀.₂₅Ni₃.₅4</td>
</tr>
<tr>
<td>850</td>
<td>33.35 (0.13)</td>
<td>1.62 (0.03)</td>
<td>64.25 (0.19)</td>
<td>99.23 (0.24)</td>
<td>La₀.₇₉Mg₀.₂₅Ni₃.₅3</td>
</tr>
<tr>
<td>870</td>
<td>33.83 (0.14)</td>
<td>1.60 (0.04)</td>
<td>63.46 (0.05)</td>
<td>98.89 (0.15)</td>
<td>La₀.₇₉Mg₀.₂₅Ni₃.₅0</td>
</tr>
<tr>
<td>900</td>
<td>33.11 (0.40)</td>
<td>1.61 (0.02)</td>
<td>63.94 (0.55)</td>
<td>98.56 (0.70)</td>
<td>La₀.₇₉Mg₀.₂₅Ni₃.₅8</td>
</tr>
</tbody>
</table>
La–Mg–Ni. The compositions correspond to the microcompositions (the probe size is about 1 μm³) obtained at the sample surfaces. Almost all measured points are located on a straight line corresponding to a constant La composition in the range 16–17 at. %.

Fig. 2 (a) shows the XRD patterns for the various La₀.₈₅Mg₀.₁₅Ni₃.₈ samples. For the one synthesized at 810 °C, the XRD pattern can be indexed with three phases: rhombohedral Gd₂Co₇-type (JCPDS 27-1107) La₃MgNi₁₄ (hereinafter 2:7R, 30 wt.%), hexagonal Pr₅Co₁₉-type (JCPDS 42-1198) La₄MgNi₁₉ (5:19H, 23 wt.%) and rhombohedral Ce₅Co₁₉-type (JCPDS 26-1084) La₄MgNi₁₉ (5:19R, 43 wt.%). A small amount of hexagonal LaNi₅ (JCPDS 50-0777) phase (4 wt%) is also observed. When the SPS temperature augments a new peak (*) at 2θ = 31.34° which cannot be assigned to the above indicated phases is observed, and its intensity increases with the SPS temperature, see Fig. 2(b). This peak can be assigned to the rhombohedral La₅MgNi₂₄ phase with space group R-3m. To verify this hypothesis, this phase was introduced in the pattern refinement of the sample synthesized at 900 °C, and the Rietveld analysis (Fig. 3) leads to 75 wt.% of this La₅MgNi₂₄ phase in this sample. All diffraction patterns have been refined assuming the possible presence of at least 6 phases (2:7R and H; 5:19R and H; 1:4R and 1:5H) and the phase abundances as determined from the Rietveld analysis are reported in Fig. 4. As concerns the crystal structure of the La₅MgNi₂₄ phase, it is found that the Mg atoms share preferentially with the lanthanum ones lying in the 6c sites within the R₅M₇ Laves phase layer. To obtain reliable data for the 2:7 and 5:19 phases, the atomic positions were refined for the samples synthesized at 810 °C, for which their abundances are significant, but they were kept fixed for refinements at higher temperatures. The crystal parameters of the LaNi₅ phase were fixed to values reported in Ref. [19]. During the Rietveld refinement, variations of the Mg occupation rate on the La site bring almost no change on the reliability factors. According to the EPMA results and to other previous reports[7,20], this parameter was not refined for all the phases (see Section 4). The refined structural parameters for the La₅MgNi₂₄ phase are listed in Table 2.

In Fig. 5 are reported the PCT curves measured at 40 °C after five cycles of activation. All samples absorb hydrogen up to 1.1 H/M. The plateau of the sample synthesized at 810 °C is rather sloppy and the plateau pressure is close to 0.1 MPa. For the samples synthesized at higher temperatures, the plateaus around 0.08 MPa in absorption are flatter and more adapted to the electrochemical application. A reversible capacity within the practical window for open cell application of 1.3 wt.% was found for all synthesized compounds, which corresponds to an electrochemical capacity of 350 mAh g⁻¹. Fig. 6 shows the electrochemical cycling behavior measured at 25 °C for the different compounds. For the compound synthesized at 810 °C, a maximum capacity of 350 mAh g⁻¹ is reached at the third cycle and remains almost constant for the following ones. For the compounds synthesized at 870 °C and 900 °C, a maximum capacity of 345 mAh g⁻¹ is obtained at the first cycle and then decreases smoothly to 310 mAh g⁻¹ at the 10th cycle (see the inset in Fig. 6). After this point, the fast cycling regime is applied (see Section 2) and the decreasing capacity rates are the same for all samples.

Fig 7 shows the XRD pattern of the sample synthesized at 900 °C and hydrided upto 1 H/M at the 10th hydrogenation cycle. After hydrogenation the sample holder was slowly opened in air to passivate the powder and to avoid any hydrogen desorption. Results from the Rietveld analysis are listed in Table 3. The lattice expansion of the La₅MgNi₂₄ (1:4R)
hydride phase is found isotropic with $\Delta a/a = +7.3\%$, $\Delta c/c = +7.7\%$ and $\Delta V/V = +23.92\%$. By comparison with the diffraction pattern collected on the hydrogen-free sample (Fig. 3), it is possible to estimate the cycling effect on the textural properties from the evolution of the diffraction line widths. The grain size and the strain of the main phase have been obtained by analyzing the diffraction peak function profile "pseudo-Voigt Thompson–Cox-Hastings". The instrument contribution was introduced, and the crystalline grains are considered as spheres. The grain size of the La$_5$MgNi$_{24}$ (1:4R) hydride phase is reduced from 95 nm for the starting materials to 50 nm after 10 cycles and the strain increases from 0.04% to 0.11%.

4. Discussion

In the La–Ni binary system, the LaNi$_3$ phase is reported to exist to 810°C with PuNi$_3$-type (1:3R) structure [21]. The La$_2$Ni$_7$ compound is reported to exist up to 970°C with the Ce$_2$Ni$_7$-
type (2:7H) structure [22–24]. The La₅Ni₁₉ compound is reported only in a small range of temperature from 950 ºC to 1000 ºC with Ce₂Co₇-type (5:19R) structure. It decomposes into LaNi₅ and LaNi₅ at lower temperature [25,26]. A recent study [25] has shown that the La₅Ni₁₉ phase crystallizes also in the hexagonal 2H-type structure (space group p6₃/mmc, 5:19H). No LaNi₅ phase was found so far in the binary system. In the ternary system La–Mg–Ni, (La, Mg)₅Ni₁₉ compound as well as (La, Mg)₆Ni₂₁ crystallize in both hexagonal and rhombohedral structures. Furthermore, the temperature formation of the three phases (La, Mg)₅Ni₁₉, (La, Mg)₆Ni₂₁ and (La, Mg)₆Ni₁₉ is lowered due to the presence of Mg [2,27]. The (La, Mg)₅Ni₁₉ remains the main phase for the samples annealed at 800 ºC [20], 900 ºC [25], 950 ºC [26] and 1000 ºC [20]. That suggests that this ternary phase is stable in a larger range of temperature than for the binary system. In the present work, the phases (2:7); (5:19); (1:4) and (1:5) coexist for all samples. The phase fraction evolves significantly with the SPS temperature (Fig. 4).

Firstly, the amount of the binary phase LaNi₅ is very small and keeps constant with the increasing sintering temperature. The global mass fraction of the (5:19) phase (both hexagonal and rhombohedral) decreases with the temperature from a major phase at 810 ºC (50 wt.%) to a minor one at 900 ºC (14 wt.%). On the other hand, the abundance of the (1:4) phase increases with temperature and becomes predominant (75 wt.%) at 900 ºC. This suggests that the (1:4) phase forms at higher temperature than the (2:7) and (5:19) phases.

Spark Plasma Sintering (SPS) technique uses a direct pulsed current with uniaxial pressure to primarily sinter powders. During the process spark plasma can be formed when electric energy in a pulse shape is directly discharged when electric energy in a pulse shape is directly discharged into the gaps between powders, which work as the heat resistor for sintering. Compared with other commonly used techniques, this method ensures a very rapid heating rate and mass transfer speed. The sample is made in a short period at relatively low temperature, and the technique avoids the volatilization of some elements with low melting point (Mg, in our case). So, SPS is suitable to prepare alloys and intermetallic compounds with low cost efficiency, shorter time and better control of the phase composition. In the present work, the La₅MgNi₁₉ phase has been synthesized at 810 ºC, lower than the temperature employed by powder metallurgy (900 ºC) [25]. Furthermore, the chemical analysis shows that the Mg losses during the synthesis process are very few, much less than the value anticipated from the powder metallurgy technique. Our results show that the SPS technique can be used for the synthesis of new generation of La–Mg–Ni type compounds with superstructures.

In Fig. 1, a tentative phase diagram has been represented within the temperature range 810–900 ºC. According to the literature data, one expects that the binary phases LaNi₅, La₅Ni₁₉ and La₅Ni₁₉ can form an extension in the ternary domain assuming a solid solution between LaNi₅ and MgNi₂ (in agreement with an increasing value of n (0 ≤ n < ∞) for the stacking model [RₗM₉]ₙ[RₗM₉]ₙ). It is commonly admitted that Mg cannot substitute La within the [LaNi₅] layers according to the fact that the solution of Mg in the La₅Ni₁₉ binary phase does not exist. On the other hand Mg can substitute La within the Laves phase layers assuming that MgNi₂ exists as a stable Laves phase compound. Accordingly, if one supposes that all the La atoms lying into the [La₅Ni₁₉] layers can be replaced by Mg, the upper solution limit is given by a line connecting LaNi₅ and MgNi₂ (see short dashed line in Fig. 1) and leading to the following compositions: LaMg₉Ni₁₅ (1:3), LaMg₉Ni₂₇ (2:7) and LaMg₉Ni₃₉ (5:19). However, except for LaMg₅Ni₁₉ [1], the other two compounds have never been reported. The upper values reported so far for the (5:19) and (2:7) phases are La₅MgNi₁₉ [25] and La₅MgNi₃₉ [26,20,28] respectively.

The peculiar case of the 1:4 phase should be discussed separately. Firstly, it was not reported for the binary La₅Ni₁₉ compound. However, in the present work a stable ternary compound La₅MgNi₃₄ has been obtained beside the other reported compounds. One hypothesis could be the stabilization of this ternary phase by Mg addition. In a previous work, the same structure has been observed for the composition La₅Mg₇Ni₃₂ (Mn, Al)₀₂ in the La₅Mg₇Ni₃₂–xCo₂₃ (Mn, Al)x (x = Pr, La, Y, 0 ≤ x ≤ 0.4) alloys [7]. It was suggested that the preferential occupations of Mg and Al in particular sites concur to the formation and stabilization of this structure.

The main striking feature of Fig. 1 is the alignment of the composition data points along an almost constant La ratio around 16–17 at.%. This can be understood if one considers (i) the stacking model and (ii) the limited magnesium substitution rate within the Laves phase layers. The stacking model is therefore [La₂₋₂,MgₙNi₃₉]n [1] and the general formula can be written as La₅₋₂₋₂MgₙNi₃₉x for which the La ratio in at.% is equal to [n−2−z]/[6(n+1)]. This ratio will remain constant only if z = 1 for which the ratio is then equal to 1/6 (i.e. 16.67%) whatever the value of n will be. This is typically what is observed in Fig. 3 and in good agreement with literature data. In previous Hayakawa’s works [20], EDX and diffraction analyses of the (La, Mg)₂Ni₁₇ and (La, Mg)₂Ni₁₉ phases have demonstrated that half of the La sites in the [La₅Ni₁₉] layer are occupied by Mg leading to an atomic ratio between La and Mg equal to 1 in this layer. They suggest a narrow solid-solution range for Mg for these structures. Our results confirm the suggestion of Hayakawa that Mg replaces half of the La atoms in the Laves phase layer. The general formula for this series of compounds can then be expressed by [LaMgₙNi₃₉] + n[LaNi₅], i.e., La₅₋₄₋₄MgₙNi₃₉ for n = 2, La₅Mg₉Ni₁₉ for n = 3 and

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>R_p</th>
<th>R_Bragg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:4R</td>
<td>R-3m</td>
<td>5.344</td>
<td>1</td>
<td>6.322</td>
<td>2</td>
<td>1</td>
<td>60</td>
<td>9.53</td>
<td>8.37</td>
</tr>
</tbody>
</table>

| La | 6c1 | 0 | 0 | 0.0327(2) | 1 |
| Mg | 6c2 | 0 | 0.0970(2) | 1 |
| Ni | 6c3 | 0 | 0.1572(2) | 0.5 |
| Mg | 6c4 | 0 | 0.2334(3) | 1 |
| Ni | 6c5 | 0 | 0.2994(3) | 1 |
| Mg | 6c6 | 0 | 0.3662(3) | 1 |
| Ni | 6c7 | 0 | 0.4318(3) | 1 |
| Ni | 6c8 | 0.50000 | 0 | 1 |
| Ni | 6c9 | 0.494(2) | --x | 0.0653(2) | 1 |
| Ni | 6c10 | 0.494(2) | --x | 0.1334(2) | 1 |
La₅MgNi₂₄ for n = 4. This result is confirmed by DFT calculation [29], the authors claim that in the pseudo-binary (La, Mg)Ni system the compounds with half of the La site filled by Mg in the Laves phase units are stable. Recently, Si et al. have reported similar results in the (Ca₂/₃Mgₓ/₃)₂Ni₇ compounds, they found that the maximum solid solubility of Mg in the (Ca, Mg)₂Ni₇ phase is about x = 0.5 [30]. However, this rule does not apply for n = 0 and 1 for which the replacement of La by Mg systems seems possible up to z = 2 leading to the compounds MgNi₂ for n = 0 and LaMg₂Ni₉ for n = 1. It is worth to note that for n = 0, depending on z, the structure changes from tetragonal La₃Ni₄₅type for z = 0 (with 12.5 at.% La vacancies) [31], to cubic MgCu₄Sn-type for z = 0.44 or 1 [32], then hexagonal MgNi₂-type for z = 2 [33].

Another important point of the Fig. 1 is that for the sample synthesized at 810 °C, the pointed compositions lay on the line between La₅MgNi₂₄ and La₅MgNi₂₄ which indicates that the samples contains mainly the R₅M₁₉ and R₂M₇ phases. When the SPS temperature increases, the RM₄ phase becomes more stable than the R₅M₁₉ and R₂M₇ phases. The R₅M₁₉ and R₂M₇ phases have a tendency to decompose into the RM₄ phase and RM₂ phase, this explains the pointed composition at lower stoichiometry (lower than RM₃). The RM₂ phase was not indexed in the X-ray diffraction pattern due to its small quantity and the multi-phase nature of the samples.

Actually, the distance between La-sites is shorter (0.32 nm) in the [La₂Ni₄] layer than in the [LaNi₅] layer (0.39 nm). Considering the smaller radii of Mg (1.60 Å) compared to La (1.87 Å), the occupation of Mg on the La site in the [La₂Ni₄] layer, reduces the mismatch between [La₅Ni₄] and [LaNi₅] layers and contribute to stabilizing the stacking structure. The structures are represented in the Fig. 8. These compositions do not change with the heat treatment temperature (here the SPS temperature). This result can be confirmed by the invariance of the cell parameters of the different phases with the SPS temperature. Fig. 9 plots the cell parameters a and c/layer number (for comparison we divide c by the number of layers in the structure; 2(n + 1) for the hexagonal structure, 3(n + 1) for the rhombohedral structure) obtained from the Rietveld analyses as function of the SPS temperature.

Regarding hydrogen sorption capacity, it is observed that it increases with the SPS temperature treatment (Fig. 5). According to the phase fraction reported in Fig. 4, the La₅MgNi₂₄ phase is the main phase and it can be concluded this phase is more capacitive that the other ones. As concerns the PCT curves, though the samples consist of several coexisting phases, flat plateaus are observed indicating that the equilibrium pressures for all hydrides phases (1:4, 5:19 and 2:7) are very close to each other probably due to their very similar crystal structure and cell volume according to Fig. 9.

For the maximum electrochemical discharge capacity, no difference was found between the alloys synthesized at 810 °C.
and 900 °C. In contrast, the cyclic stability shows a different behavior. The sample for which the R5M19 phase is the main phase has a better cycling stability than the sample containing large amount of the La5MgNi24 phase.

It is known that the cycling capacity decay of the metal-hydride electrode is influenced by two factors: the surface passivation due to the oxidation of active components and the pulverization due to the volume expansion of the hydride phase. The cycle stability of the binary compounds LaNi\textsubscript{x} with superstructure is generally smaller than that of classical LaNi\textsubscript{5}-type compounds\[25,34,36\]. This difference is caused by the poor stability of the La2Ni4 and "contracted" LaNi\textsubscript{5} subunits. It was shown that La substitution by Mg in the Laves layer reduces the "mismatch" between the Laves and LaNi\textsubscript{5} layers and stabilizes the superstructure\[6,27\]. The ternary phases have better cyclic stability than their corresponding binary ones \[25,28\]. Up to now, systematic studies on the cyclic stabilities of the ternary superstructure phases are still missing.

The structure of the (La, Mg)\textsubscript{n}Ni\textsubscript{3} and (La, Mg)\textsubscript{n}Ni\textsubscript{19} hydride phases have been studied by neutron and in situ X-ray diffraction \[26,34\]. It is reported that hydrogen occupies tetrahedral sites in the R3\textsubscript{m} unit and both tetrahedral and octahedral sites in the RM\textsubscript{3} ones. In the case of La3MgNi\textsubscript{14} (Ce2Ni\textsubscript{7}-type phase 2:7H\textsubscript{1}), the expansion due to hydrogen absorption is anisotropic with $\Delta a/a = +7.37\%$ and $\Delta c/c = +9.58\%$. The anisotropic effect for the Pr5Co19-type (5:19H\textsubscript{1}) phase is less pronounced with $\Delta a/a = +7.3(0)\%$ and $\Delta c/c = +8.8(0)\%$. In the present work, the lattice expansion of the La5MgNi24 phase is rather isotopic with $\Delta a/a = +7.3(1)\%$ and $\Delta c/c = +7.7(1)\%$. It shows that the anisotropy effect decreases with the number of the LaNi\textsubscript{5} layer present in the structure. It is confirmed that this anisotropic effect is mainly due to the anisotropic expansion of the [LaMgNi\textsubscript{3}] subunits \[26,34\] and Zhang et al. have shown that the amorphization in the RNi\textsubscript{3} system is mainly related to the poor stability of the Laves phase subunits in the structure \[37\]. Hence, it is reasonable to

<table>
<thead>
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<th>Synthesized sample</th>
<th>Phase</th>
<th>1:4 R</th>
<th>1:5 H</th>
<th>5:19 R</th>
<th>5:19 H</th>
<th>2:7 R</th>
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<tr>
<td>S.G.</td>
<td>R-3m</td>
<td>P6\textsubscript{3}mmm</td>
<td>R-3m</td>
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<tr>
<td>a (Å)</td>
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<td>5.0296(f)</td>
<td>5.0367(6)</td>
<td>5.034(1)</td>
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<tr>
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<td>3.9876(f)</td>
<td>48.419(6)</td>
<td>32.205(7)</td>
<td>36.22(5)</td>
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<td>V (Å\textsuperscript{3})</td>
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<td>87.359 (f)</td>
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<td>706.9(3)</td>
<td>785.7(7)</td>
<td></td>
</tr>
<tr>
<td>Grain size (nm)</td>
<td>95(5)</td>
<td>6</td>
<td>11</td>
<td>7</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Abundance (wt%)</td>
<td>72</td>
<td>5.4004 (3)</td>
<td>5.369(3)</td>
<td>5.405(1)y</td>
<td>5.402(1)x</td>
<td>5.377(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1640.0(2)</td>
<td>4.264(3)</td>
<td>52.33(1)</td>
<td>34.73(1)</td>
<td>38.36(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40(3)</td>
<td>106.5(1)</td>
<td>1323.9(5)</td>
<td>877.7(3)</td>
<td>960.5(9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3 – Phase composition obtained from the Rietveld analysis of the sample synthesized at 900 °C and hydrided at 10th hydrogenation cycle with comparison of the initial sample (standard deviation given between brackets; f, values kept fixed in the refinement).

Fig. 8 – Schematic representation of the stacking structure from $n = 1$ to 4.
La₄MgNi₁₉ as the main phase with superstructures. The new La₅MgNi₂₄ phase has been synthesized and its structure determined by XRD analysis. The alloy containing La₃MgNi₁₄, La₄MgNi₁₉, La₅MgNi₂₄ is partially caused by the anisotropic expansion of LaMgNi₄ subunits by hydrogen absorption. Therefore, the structure stability is expected to increase with the stoichiometry RNi₆ since the increasing number of RM₅ subunits in the structure allows to absorb lattice strains.

From previous works, it was shown that the La₅MgNi₂₄ phase with $S_{100} = 88\%$ [38]; La₄MgNi₁₉ phase with $S_{100} = 85.2\%$ [39]; where $S_{100} = \text{capacity at the 100th cycle/capacity at first cycle}$, have better cycle stability than the La₃MgNi₁₉ phase ($S_{100} = 60\%$) [40,41]. In the present work, the alloy containing La₅MgNi₂₄ as the main phase with $S_{100} = 86\%$ has good agreement with previous reports. The alloy contains La₄MgNi₁₉ as main phase with $S_{100} = 72\%$ has less cycling stability than La₃MgNi₁₄ and La₅MgNi₁₉, but much better than La₂MgNi₈ phase. Nevertheless, the cycle stability cannot be correlated to the anisotropic cell expansion by hydrogen absorption. There should be another parameter to take into account to explain those differences. To solve the question of the cycle stability for the superstructure compounds, more detailed studies on the structure stability are needed. Ab-initio calculation on the structure stability will be inestimable to guide experience to a successful synthesis of the new materials with high capacity and good cycle stability for the Ni/MH batteries application.

**5. Conclusion**

Our results show that the SPS technique can be used for the synthesis of new generation of La–Mg–Ni type compounds with superstructures. The new La₅MgNi₂₄ phase has been synthesized and its structure determined by XRD analysis. This phase forms at higher temperature than the R₅M₁₉ and R₇M₅ phases. This new phase belongs to the family of stacking structures of RM₅ and R₇M₅ units along the c axis, which are stabilized due to the partial substitution of Mg for La in R₇M₅ units. We have shown that this stabilization could be explained by the decrease of the “mismatch” between the RM₅ and R₇M₅ units when La is substituted by Mg in the (La, Mg)₂Ni₄ subunits. Besides, it seems that the substitution rate of Mg for La cannot pass beyond 1 atom per R₇M₅ unit. The hydrogen storage capacity as well as the electrochemical capacity is not much influenced by the SPS temperature. In contrast, the cyclic stability shows better resistance for the samples containing more R₇M₁₉ phases. To get a better understanding of the capacity decay mechanism, detailed studies of the cycled compounds adopting different superstructure are needed.

**Prime novelty statement**

I, Dr., Junxian Zhang, confirm that this manuscript is the authors’ original work and has not been published nor has been submitted elsewhere. All authors have read the manuscript and agree this statement of originality. The La–Mg–Ni ternary system has been extensively studied and for the first time the La₅MgNi₂₄ phase prepared by SPS technique is reported. The crystal structure and phase composition have been analyzed by X-ray diffraction and EPMA. The effect of the SPS temperature on the phase formation, the correlation between the cycling stability and phase composition have been investigated.

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**References**