(La$_{1.66}$Mg$_{0.34}$)Ni$_7$-based alloys: Structural and Hydrogen Storage Properties

Zhijie Gao*, Huiming Zhang

Department of Chemistry and Chemical Engineering, Binzhou University, Binzhou 256600, PR China
*E-mail: gaozhijie1983@126.com

Received: 6 November 2015 / Accepted: 25 November 2015 / Published: 1 January 2016

The structural and hydrogen storage properties of (La$_{1.66}$Mg$_{0.34}$)Ni$_7$-based alloys (i.e., A$_2$B$_7$-type) with a main structure (hexagonal Ce$_2$Ni$_7$-type) are investigated in this study. In Ce$_2$Ni$_7$-type structure, upon hydrogen the approximately single phase sample of the intermetallic compound with (La$_{1.66}$Mg$_{0.34}$)Ni$_7$ expands isotropically, in contrast to the Mg free phase and La$_{0.63}$R$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$ alloy. A decrease in the A-atomic radius and an increase in the B-atomic radius stabilize the metal sublattice and increase the reversible hydrogen storage capacity. The unit cell parameters in La$_{0.63}$R$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$ alloy is almost no change during hydrogenation and the amorphous effect is very slight, compared to pure La$_2$Ni$_7$, which easily become amorphous upon hydrogen absorption-desorption cycling.

Keywords: Rare earth elements, Alloy structure, Unit cell volume, Equilibrium pressure, Electrochemical properties

1. INTRODUCTION

Hydrogen storage alloys have been attached more and more importance to application with “Hydrogen Energy” and research with “Ni/MH battery” put forward [1-3]. Rare-earth-based AB$_5$-type alloy and Zr-based Laves phase alloy have been commercialized successfully as Ni/MH secondary cell negative materials [4,5], but low capacity of AB$_5$-type alloy electrodes and difficult activation characteristics of Laves phase alloy electrodes limit the extensive application [6,7]. Many electrode materials are regarded as promising energy storage applications due to their powerful and reversible electrochemical redox reactions [8].

Since the use of LaMg$_2$Ni$_9$, La$_2$MgNi$_9$ and La$_3$Mg$_2$Ni$_{12}$ compounds was reported as hydrogen storage materials [9-11], ternary R-Mg-Ni (R = rare earth metals) compounds have been studied because their hydrogen storage properties are superior to corresponding binary AB$_n$ (n = 2-5).
2. EXPERIMENTAL DETAILS

2.1 Sample Preparation

(La$_{1.66}$Mg$_{0.34}$)Ni$_7$ and (L$_{1.26}$R$_{0.4}$Mg$_{0.34}$)(Ni$_{6.2}$Co$_{0.6}$Al$_{0.2}$) R=La, Ce, Pr, Nd, Y, Sm, Gd were prepared by induction melting approach at 0.4 MPa of Ar. atmosphere. The ingots were wrapped in a thallium (Ta) foil, sealed in stainless steel tubes under Ar pressure (0.1 MPa) and annealed for a week at 1173K. Due to the high vapor pressure of Mg element, 10 wt.% excess of Mg element was necessary during melting. The purity of all elements was above 99 wt.%.
2.2 Structural Characterization

The annealed alloys were crushed mechanically into powder (<38 µm) for x-ray diffraction (XRD) measurements and powder from 54 µm to 61 µm for electrode test. XRD measurements were performed on a Rigaku D/max-2400 diffractometer with Cu radiation and a power of 40 kV × 150 mA. The patterns were recorded over the range from 15° to 90° in 20 by step of 0.02°. Then the collected data were analyzed by the Rietveld method [35] using Fullproff 2K software [36] to get the lattice parameters and phase abundance.

The microscopic structure and the composition for annealed alloys were examined by Electron probe microanalyzer (EPMA-1600). After hydrogenation, the samples were examined using a transmission electron microscope (TEM, JEOL, JEM-2010, Japan) and a scanning electron microscope (SEM, JEOL, JSM-6701F, Japan) at an accelerating voltage of 8 kV.

2.3 Hydrogen Absorption and Desorption

To investigate the hydrogen storage properties of (La_{1.66}Mg_{0.34})Ni_{7}-based compounds, pressure-composition (P–C) isotherms were measured using a Sieverts-type apparatus (Beijing Nonferrous Metal Research Institute, China) at 298 K. Prior to formal measurements, powder samples were heated in a vacuum at 373 K for 2 h and then activated by repeatedly hydriding–dehydriding at 333 K three times.

3. RESULTS AND DISCUSSION

3.1 Alloy crystal structure

Fig. 1 shows the XRD patterns for (La_{1.66}Mg_{0.34})Ni_{7} and La_{0.63}R_{0.2}Mg_{0.17}Ni_{3.1}Co_{0.3}Al_{0.1} (R=La, Ce, Pr, Nd, Y, Sm, Gd) alloys. Fig. 2 shows the Rietveld refinement patterns of (La_{1.66}Mg_{0.34})Ni_{7} and La_{0.63}R_{0.2}Mg_{0.17}Ni_{3.1}Co_{0.3}Al_{0.1} (R = La, Gd) alloy, respectively. Structure characteristics of different R-substituted alloys are tabulated in Table 1. Based on the XRD data, the crystal structure of (La, Mg)$_2$Ni$_7$ seems to retain the hexagonal Ce$_2$Ni$_7$-structure type. The back scattered electron (BSE) image of La$_{0.63}$R$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$ (R=La, Pr, Y, Gd) and are shown in Fig 3. A light grey area (α) and black area (β) can be seen in Fig 3 ((a) - (d)). The WDS analyses in Fig 3 show that the light grey (α) and black area (β) correspond to A$_2$B$_7$- and AB$_5$-type phase, respectively. The results are consistent with those obtained from XRD.

The crystallographic parameters of Ce$_2$Ni$_7$ unit cell for the alloy of (La$_{1.66}$Mg$_{0.34}$)Ni$_7$ are tabulated in Table 2, according to Rietveld analysis. The Rietveld refinements show that Mg partly substitutes La, exclusively in the LaNi$_2$ slabs (4f site) and occupies statistically ~35% of the available sites. The well crystalline phase reveals close similarity to La$_2$Ni$_7$ but with reduced unit cell parameters due to the smaller magnesium and rare earth radii (see Table3). Compared to pure La$_2$Ni$_7$, the contraction of the unit cell due to the introduced Mg for (La$_{1.66}$Mg$_{0.34}$)Ni$_7$ is: $\triangle V/V = -1.6\%$ with $\triangle a/a$...
= -0.2% and $\Delta c/c = -1.3\%$, without any change of the symmetry (hexagonal, P6$_3$/mmc). For La$_{0.83}$Mg$_{0.17}$Ni$_3.1$Co$_{0.3}$Al$_{0.1}$ and La$_{0.63}$-Gd$_{0.2}$Mg$_{0.17}$Ni$_3.1$Co$_{0.3}$Al$_{0.1}$, the contraction of the Ce$_2$Ni$_7$ (hexagonal, P6$_3$/mmc) unit cell is: $\Delta V/V = -0.97\%$ with $\Delta c/c = -1.1\%$, $\Delta V/V = -2.2\%$ with $\Delta a/a = -0.4\%$ and $\Delta c/c = -1.5\%$, respectively. Because of the large difference in the atomic radii (La (1.877 Å) and Gd (1.602 Å), Ni (1.24 Å) and Al (1.43 Å)) and selective occupation of Mg in the 4f sites, Co and Al in the Ni sites, the main contraction proceed in the AB$_2$ layers. These results are in agreement with published ones [20, 32, 37, 38]. So we hypothesize that R only occupies the 4f sites and improves the contraction in the AB$_2$ slabs, this is one of the reason why La$_{0.63}$R$_{0.2}$Mg$_{0.17}$Ni$_3.1$Co$_{0.3}$Al$_{0.1}$ (R = Pr, Nd, Sm, Gd, Y) exhibits good electrochemical properties [32].

Table 1. Characteristics of phases for (La$_{1.66}$Mg$_{0.34}$)Ni$_7$ and La$_{0.63}$R$_{0.2}$Mg$_{0.17}$Ni$_3.1$Co$_{0.3}$Al$_{0.1}$ alloys.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Space Group</th>
<th>Lattice constants (Å)</th>
<th>Phase abundance (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$a$</td>
<td>$c$</td>
</tr>
<tr>
<td>(La$<em>{1.66}$Mg$</em>{0.34}$)Ni$_7$</td>
<td>(La,Mg)$_2$(Ni,Co)$_7$</td>
<td>R-3m</td>
<td>5.051</td>
<td>36.399</td>
</tr>
<tr>
<td></td>
<td>(La,Mg)$_2$(Ni,Co)$_7$</td>
<td>P6$_3$/mmc</td>
<td>5.050</td>
<td>24.389</td>
</tr>
<tr>
<td></td>
<td>La(Ni,Co)$_5$</td>
<td>P6/mmm</td>
<td>5.045</td>
<td>3.980</td>
</tr>
<tr>
<td>R = La</td>
<td>(La,Mg)$_2$(Ni,Co)$_7$</td>
<td>R-3m</td>
<td>5.098</td>
<td>36.662</td>
</tr>
<tr>
<td></td>
<td>La(Ni,Co)$_5$</td>
<td>P6/mmm</td>
<td>5.061</td>
<td>24.438</td>
</tr>
<tr>
<td>R = Ce</td>
<td>(La,Mg)$_2$(Ni,Co)$_7$</td>
<td>R-3m</td>
<td>4.949</td>
<td>36.670</td>
</tr>
<tr>
<td></td>
<td>La(Ni,Co)$_5$</td>
<td>P6/mmm</td>
<td>5.032</td>
<td>24.399</td>
</tr>
<tr>
<td>R = Pr</td>
<td>(La,Mg)$_2$(Ni,Co)$_7$</td>
<td>R-3m</td>
<td>5.056</td>
<td>4.063</td>
</tr>
<tr>
<td></td>
<td>La(Ni,Co)$_5$</td>
<td>P6/mmm</td>
<td>5.338</td>
<td>37.945</td>
</tr>
<tr>
<td>R = Nd</td>
<td>(La,Mg)$_2$(Ni,Co)$_7$</td>
<td>R-3m</td>
<td>5.049</td>
<td>24.401</td>
</tr>
<tr>
<td></td>
<td>La(Ni,Co)$_5$</td>
<td>P6/mmm</td>
<td>5.019</td>
<td>3.996</td>
</tr>
<tr>
<td>R = Y</td>
<td>(La,Mg)$_2$(Ni,Co)$_7$</td>
<td>R-3m</td>
<td>5.048</td>
<td>24.392</td>
</tr>
<tr>
<td></td>
<td>La(Ni,Co)$_5$</td>
<td>P6/mmm</td>
<td>5.019</td>
<td>3.998</td>
</tr>
<tr>
<td>R = Sm</td>
<td>(La,Mg)$_2$(Ni,Co)$_7$</td>
<td>R-3m</td>
<td>5.029</td>
<td>24.302</td>
</tr>
<tr>
<td></td>
<td>La(Ni,Co)$_5$</td>
<td>P6/mmm</td>
<td>5.016</td>
<td>4.013</td>
</tr>
<tr>
<td>R = Gd</td>
<td>(La,Mg)$_2$(Ni,Co)$_7$</td>
<td>R-3m</td>
<td>5.035</td>
<td>4.030</td>
</tr>
<tr>
<td></td>
<td>La(Ni,Co)$_5$</td>
<td>P6/mmm</td>
<td>5.079</td>
<td>36.541</td>
</tr>
<tr>
<td></td>
<td>(La,Mg)$_2$(Ni,Co)$_7$</td>
<td>R-3m</td>
<td>5.039</td>
<td>24.351</td>
</tr>
<tr>
<td></td>
<td>La(Ni,Co)$_5$</td>
<td>P6/mmm</td>
<td>4.995</td>
<td>4.089</td>
</tr>
</tbody>
</table>
Figure 1. XRD patterns for (La$_{1.66}$Mg$_{0.34}$)Ni$_7$ and La$_{0.63}$R$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$ alloys.

Figure 2. Rietveld refinement patterns for (La$_{1.66}$Mg$_{0.34}$)Ni$_7$ and La$_{0.63}$R$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$ alloy: (A) (La$_{1.66}$Mg$_{0.34}$)Ni$_7$ (B) R = La, (C) R = Gd.

Table 2. Crystallographic parameters of (La$_{1.66}$Mg$_{0.34}$)Ni$_7$ alloy with space group P6$_3$/mmc.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B$_{iso}$</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>La 1</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
<td>0.02698(8)</td>
<td>1.03(6)</td>
<td>0.66(1)</td>
</tr>
<tr>
<td>La 2</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
<td>0.17108(6)</td>
<td>0.98(4)</td>
<td>1.00(1)</td>
</tr>
<tr>
<td>Mg 1</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
<td>0.02698(8)</td>
<td>1.03(-)</td>
<td>0.35(-)</td>
</tr>
<tr>
<td>Ni 1</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.9(1)</td>
<td>1.00(-)</td>
</tr>
<tr>
<td>Ni 2</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.1678(1)</td>
<td>0.98(7)</td>
<td>1.00(-)</td>
</tr>
<tr>
<td>Ni 3</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
<td>0.8329(1)</td>
<td>0.61(6)</td>
<td>1.00(-)</td>
</tr>
<tr>
<td>Ni 4</td>
<td>6h</td>
<td>0.8326(8)</td>
<td>0.665(2)</td>
<td>1/4</td>
<td>0.50(6)</td>
<td>1.00(-)</td>
</tr>
<tr>
<td>Ni 5</td>
<td>12k</td>
<td>0.8330(5)</td>
<td>0.666(1)</td>
<td>0.08486(6)</td>
<td>0.84(4)</td>
<td>1.00(-)</td>
</tr>
</tbody>
</table>
Figure 3. Back scattered electron images for La\textsubscript{0.63}R\textsubscript{0.2}Mg\textsubscript{0.17}Ni\textsubscript{3.1}Co\textsubscript{0.3}Al\textsubscript{0.1} alloys (a) R = La (b) R = Pr (c) R = Y (d) R = Gd.

Table 3. Comparison of selected crystallographic parameters for chosen hexagonal Ce\textsubscript{2}Ni\textsubscript{7}-type compounds in La-Ni, La-Mg-Ni and La-R-Mg-Ni systems.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Compound</th>
<th>La\textsubscript{2}Ni\textsubscript{7} [29]</th>
<th>La\textsubscript{1.66}Mg\textsubscript{0.34}Ni\textsubscript{7} [30]</th>
<th>La\textsubscript{1.5}Mg\textsubscript{0.5}Ni\textsubscript{7}</th>
<th>La\textsubscript{0.83}Gd\textsubscript{0.2}Mg\textsubscript{0.17}Ni\textsubscript{3.1}Co\textsubscript{0.3}Al\textsubscript{0.1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.058</td>
<td>5.0285</td>
<td>5.050</td>
<td>5.061</td>
<td>5.039</td>
</tr>
<tr>
<td>V (Å\textsuperscript{3})</td>
<td>547.47</td>
<td>530.42</td>
<td>538.699</td>
<td>542.148</td>
<td>535.507</td>
</tr>
<tr>
<td>V\textsubscript{AB5} (Å\textsuperscript{3})</td>
<td>177.37</td>
<td>175.77</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V\textsubscript{AB2} (Å\textsuperscript{3})</td>
<td>96.35</td>
<td>89.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Δa/a (%)</td>
<td>-0.6</td>
<td>-0.2</td>
<td>0.06</td>
<td>-0.4</td>
<td></td>
</tr>
<tr>
<td>Δc/c (%)</td>
<td>-2.0</td>
<td>-1.3</td>
<td>-1.1</td>
<td>-1.5</td>
<td></td>
</tr>
<tr>
<td>ΔV/V (%)</td>
<td>-3.1</td>
<td>-1.6</td>
<td>-0.97</td>
<td>-2.2</td>
<td></td>
</tr>
</tbody>
</table>
3.2 Thermodynamic (P-C isotherm) measurements

The single plateau behaviour is clearly seen in the absorption and desorption isotherms at 298K (Fig. 4). It can be seen that the absorption-desorption plateau became flatter and 298K (Fig. 4). It can be seen that the absorption-desorption plateau became flatter and isotherms are not horizontal, it is obvious that the plateau slope gradually decrease from (La1.66,Mg0.34)Ni7 to Gd-substituted alloy. Similar observations have been made by Oesterreicher et al. [39], who noticed that La2Ni7H10 decomposes with hydrogen desorption. Such disproportionation also made impossible measurements of the thermodynamic data for the chemically related LaNi3-H and LaNi2-H systems, where hydrides easily become amorphous and, later, disproportionate. This can be further confirmed by the result of TEM image shown in Fig. 5. Fig. 5(A) and (B) show TEM images of La1.66Mg0.34Ni7H6.4 and La0.63Gd0.2Mg0.17Ni3.1Co0.3Al0.1H8.8, respectively. Both of them exhibit amorphous phenomenon, but the amorphous effect of La0.63Gd0.2Mg0.17Ni3.1Co0.3Al0.1 alloy is more slight.

In addition, the hydrogen content also gradually increased from 0.98 wt.% to 1.353 wt.. In our work, the maximum hydrogen capacity at 298K is slightly lower than for La1.5Mg0.5Ni7 at 298K [30].

![Figure 4. P-C isotherms of (La1.66,Mg0.34)Ni7 and La0.63R0.2Mg0.17Ni3.1Co0.3Al0.1 (R = La, Gd) alloys at 298K.](image)

![Figure 5. TEM image of La1.66Mg0.34Ni7H6.4 and La0.63Gd0.2Mg0.17Ni3.1Co0.3Al0.1H4.4 hydrides.](image)
3.3 Study of the hydride

The hydrogenation of the (La$_{1.66}$Mg$_{0.34}$)Ni$_7$ and La$_{0.63}$Ro$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$ (R = La, Gd) alloy resulted in the formation of the hydride with the composition of La$_{1.66}$Mg$_{0.34}$Ni$_7$H$_{6.4}$, La$_{0.83}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$H$_{3.55}$, and La$_{0.63}$Gd$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$H$_{4.4}$, as follows from the PCT isotherm at 298K (Fig. 4). The hydrogenation is accompanied by isotropic expansion of the La$_{1.66}$Mg$_{0.34}$Ni$_7$H$_{6.4}$ unit cell, \( \Delta a/a = 7.3\% \) and \( \Delta c/c = 9.1\% \). These values are close to those observed for the formation of the La$_{1.5}$Mg$_{0.5}$Ni$_7$H$_{9.3}$ of the filled Ce$_2$Ni$_7$ type of structure [30] and are in sharp contrast with the values for the hydride of the isostructural non-substituted La$_2$Ni$_7$ alloy, which expands anisotropically [29] (see Table 4). The isotropic expansion of the unit cell of La$_{1.66}$Mg$_{0.34}$Ni$_7$ indicates that the hydrogenation leads to an even distribution of hydrogen through all the slabs of the structure, similarly as it has been observed for La$_{1.5}$Mg$_{0.5}$Ni$_7$ [30]. This is in contrast to anisotropic hydrides, where only Laves phase-type slabs accommodate hydrogen, leaving the CaCu$_5$-type layers unexpanded. However, when Ni is partially replaced by Co and Al, the hydrogenation is accompanied by anisotropic expansion in La$_{0.63}$Gd$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$ unit cell: \( \Delta a/a = 3.6\% \) and \( \Delta c/c = -3.5\% \). For La$_{0.63}$Gd$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$ unit cell, the hydrogenation is accompanied by slight isotropic contraction, \( \Delta a/a = -0.2\% \) and \( \Delta c/c = -0.8\% \). This value is very close to the isostructural non-substituted La$_2$Ni$_7$ alloy. So La$_{0.63}$Gd$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$H$_X$ is in contrast to other hydrides, where the expansion of unit cell is large after hydrogenation.

Fig. 6 (A) and (B) shows the XRD patterns for hydrides and the Rietveld refinement patterns of La$_{0.63}$Gd$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$H$_{4.4}$, respectively. SEM are employed to investigate the surface morphology of the La$_{1.66}$Mg$_{0.34}$Ni$_7$H$_{6.4}$, La$_{0.83}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$H$_{3.55}$, and La$_{0.63}$Gd$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$H$_{4.4}$. Fig. 7 (A) – (C) show the SEM images of above three hydrides, respectively. Average particle size is in the order: La$_{1.66}$Mg$_{0.34}$Ni$_7$H$_{6.4}$ < La$_{0.83}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$H$_{3.55}$ < La$_{0.63}$Gd$_{0.2}$Mg$_{0.17}$Ni$_{3.1}$Co$_{0.3}$Al$_{0.1}$H$_{4.4}$. The results are consistent with those obtained from unit cell volume (\( \Delta V/V \)).

Table 4. Comparison of selected crystallographic parameters for chosen hexagonal Ce$_2$Ni$_7$-type hydrides in La-Ni, La-Mg-Ni and La-R-Mg-Ni systems.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Compound</th>
<th>La$_2$Ni$_7$ [29]</th>
<th>La$_2$Ni$<em>7$D$</em>{0.5}$ [29]</th>
<th>La$<em>{1.5}$Mg$</em>{0.5}$Ni$<em>7$H$</em>{3.5}$ [30]</th>
<th>La$<em>{1.66}$Mg$</em>{0.34}$Ni$<em>7$H$</em>{6.4}$</th>
<th>La$<em>{0.83}$Mg$</em>{0.17}$Ni$<em>{3.1}$Co$</em>{0.3}$Al$<em>{0.1}$H$</em>{3.55}$</th>
<th>La$<em>{0.63}$Gd$</em>{0.2}$Mg$<em>{0.17}$Ni$</em>{3.1}$Co$<em>{0.3}$Al$</em>{0.1}$H$_{4.4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.058</td>
<td>4.9534</td>
<td>5.4121</td>
<td>5.4151</td>
<td>5.2388</td>
<td>5.0457</td>
<td></td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>547.47</td>
<td>628.52</td>
<td>674.48</td>
<td>673.95</td>
<td>566.917</td>
<td>540.325</td>
<td></td>
</tr>
<tr>
<td>V$_{AB5}$ (Å$^3$)</td>
<td>177.37</td>
<td>171.96</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>V$_{AB2}$ (Å$^3$)</td>
<td>96.35</td>
<td>142.30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>( \Delta a/a ) (%)</td>
<td>-</td>
<td>-2.1</td>
<td>7.63</td>
<td>7.3</td>
<td>3.6</td>
<td>-0.2</td>
<td></td>
</tr>
<tr>
<td>( \Delta c/c ) (%)</td>
<td>-</td>
<td>19.7</td>
<td>9.77</td>
<td>9.1</td>
<td>-3.5</td>
<td>-0.8</td>
<td></td>
</tr>
<tr>
<td>( \Delta V/V ) (%)</td>
<td>-</td>
<td>14.8</td>
<td>25.2</td>
<td>25.6</td>
<td>3.6</td>
<td>-1.3</td>
<td></td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

A systematic investigation of the structural and hydrogen storage properties of (La$_{1.66}$Mg$_{0.34}$)Ni$_7$-based compounds was conducted in this study. Some conclusion can be summarized:

1) The (La$_{1.66}$Mg$_{0.34}$)Ni$_7$-based alloy is composed of a hexagonal phase (Ce$_2$Ni$_7$) and accompanied by minor impurity phases LaNi$_5$, 3R-Gd$_2$Co$_7$.

2) These changes are caused by partial replacement of La by R and include:

   (a) Increase of the reversible hydrogen storage capacity;

   (b) Absence of amorphous phenomenon and disproportionation of the metal matrix on cycling of hydrogenation and decomposition because of the stabilisation of the metal sublattice by R;

   (c) Change of the mechanism of hydrogenation from an “anisotropic” hydride to an “isotropic” one;
(d) Little change of the unit cell parameters between La_{0.66}R_{0.2}Mg_{0.17}Ni_{3.1}Co_{0.3}Al_{0.1}H_x and non-substituted La_2Ni_7 alloy.

The present work contributes to the design of new low-Mg R-Mg-Ni materials with higher hydrogen discharge capacities for technological applications such as electrode materials in rechargeable Ni/MH batteries.

**ACKNOWLEDGEMENTS**

This work was supported by the National Nature Science Foundation of China (No. 50941019), the Nature Science Foundation of Shandong Province (No. ZR2014EMP012), the Nature Science Foundation of Shandong Province (No. ZR2015PB007) and the Science and Technology Development Plan of Bingzhou (No. 2014ZC0216).

**References**

181.

© 2016 The Authors. Published by ESG (*www.electrochemsci.org*). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).