Crystal Structures of La–Mg–Niₙ (x = 3–4) System Hydrogen Storage Alloys

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The new alloys of the La–Mg–Ni (Ni/(La + Mg) = 3–4) system absorb and desorb hydrogen at room temperature, and their hydrogen storage capacities are greater than those of conventional AB₅-type alloys. We investigated the crystal structures of the La₂Mg₀.₅Ni₁₈Co₀.₅ (alloy T1) and the La₅Mg₀.₅Ni₁₉Co₁₆ (alloy T2) using ICP, SEM-EDX and XRD. We found that alloy T1 consisted of Ce₂Ni₁-type La₃Mg(Ni, Co)₁₄ and PuNi₁-type La₃Mg(Ni, Co)₁₄ phases, and alloy T2 consisted of Ce₂Ni₁-type La₃Mg(Ni, Co)₁₄ and Pr₄Co₁₉-type La₅Mg(Ni, Co)₁₉ phases. These alloy systems had layered structures and showed polytypism that originated from differences in the stacking patterns of the unit cells, which were composed of several [CaCu₅]-type layers and a single [MgZn₂]-type layer along the c-axis. The crystal structure of La₃Mg(Ni, Co)₁₄ was of a hexagonal 2H-Ce₃-Co₄-type with a = 0.5052(1) nm, and c = 2.425(3) nm. La₃Mg(Ni, Co)₁₄ had a trigonal 3R-PuNi₁-type structure with a = 0.5062(1) nm, and c = 2.4500(2) nm. La₅Mg(Ni, Co)₁₉ had a hexagonal 2H-Pr₄Co₁₉-type structure with a = 0.5042(2) nm and c = 3.2323(5) nm. In all these structures, the La-La distance of the [CaCu₅] layer was 0.38–0.40 nm and that of the [MgZn₂] layer was 0.32 nm. We also found that Mg occupied the La site in the [MgZn₂] layer. Selective occupation by Mg of the La site in the [MgZn₂] layer makes the alloy stable against repeated reaction cycles with hydrogen. The alloy system that forms this material group can be described by the general formula Laₙ₋₁MgNiₙ₋₄, where n = 0, 1, 2, 3, 4, . . .

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1. Introduction

Both La–Ni and Mg–Ni system alloys are representative hydrogen storage alloys. The La–Mg–Ni system, which is a hybrid of these two, has recently been attracting attention as a negative electrode material for Ni–MH secondary batteries, owing to its potential advantages, which include longer life, higher capacity, and environmental conformity. Kohno et al.¹³ reported that La₂MgNi₁₉, La₅Mg₂Ni₁₃, and La₃MgNi₁₄, which are new La–Mg–Ni (x = Ni/(La + Mg) = 3.0–3.5) system alloys, absorb and desorb hydrogen at room temperature. They reported that these alloys, which are partly replaced by Co, are new hydrogen storage alloys with better hydrogen absorbing and desorbing properties and better charging and discharging properties than those of LaNi₅, an existing alloy well known for its high hydrogen storage capacity at room temperature.

A partial La–Ni phase diagram for Ni = 50–100% has been proposed by Zhang et al.²³ The Laves-phase LaNi₅ shown in the diagram is reported³¹ to be metastable, and the relevant phase is a tetragonal La₀.₈₇₅Ni₂ lacking La. Additionally, the existence of La₅Ni₁₉ was reported by Yamamoto et al.³⁴ for the first time in 1997. They reported that this intermetallic compound exists only in a very narrow high temperature range not lower than 900°C. Figure 1 is a partial La–Ni phase diagram for Ni = 50–100%, constructed on the basis of these reports. Five incongruently melting intermetallic compounds, La₃Ni₁₃, La₇Ni₁₆, La₅Ni₁₃, La₇Ni₁₇, and La₅Ni₁₉, are known to exist between the congruently melting intermetallic compounds LaNi and La₅Ni₁₃. In the Mg–Ni system,³⁰ on the other hand, the existence of a Laves-phase (C₃₆-type structure) Mg₆Ni₂ intermetallic compound and a C₁₆-type structure Mg₆Ni₂ is known. Mg₆Ni₂ is well known as a hydrogen storage alloy.

Komura et al. have classified the crystal structures of complex Laves phase-based intermetallic compounds by differences in their stacking periods in terms of the basic structures of the Laves phases represented by Mg₆Cu₂, MgZn₂, and MgNi₂.⁶,⁷ Later on, they found that many polytypes can exist by conducting transmission electron microscope (TEM) observations of Sm–Co and Sm–Ni systems from viewpoints of their structural similarity to Mg-based Laves phases and of magnetic materials. These polytypes have various stacking combinations of the Laves layer and [CaCu₅]-structure layers stacked along the c-axis in the case of Sm–Co and Sm–Ni alloy systems.⁸ Khan showed that, from crystallographic research on R–T intermetallic compounds (R: rare earth metal, T: transition metal such as Fe, Co, and Ni), these intermetallic compounds form a one-dimensional long-period superstructure based on [CaCu₅]-type structure, which can be described by the general formula RTₙ, where x = (5n + 4)/(n + 2) with n = 0, 1, 2, 3, 4, . . .³⁹

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Fig. 1 Partial phase diagram of the La–Ni binary system (50–100 at% Ni).

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Kohno et al.\textsuperscript{13} reported that La–Mg–Ni ternary alloys form superlattice structures with AB\textsubscript{3} and AB\textsubscript{2} units stacked along the c-axis from the results of TEM observation. Then, they proposed a new structural model for La\textsubscript{3}Mg\textsubscript{2}Ni\textsubscript{5} hybrid-stacked with LaNi\textsubscript{3} and La\textsubscript{2}Ni\textsubscript{2} structures.

As for research on the R–Mg–Ni system hydrogen storage alloys, research has recently been conducted by Kadir et al. on a new series of ternary hydrogen storage alloys expressed by the general formula RMg\textsubscript{2}Ni\textsubscript{9} (R = rare earth metal or Ca).\textsuperscript{10–13} These compounds have a layered structure composed of a Laves structure (MgCu\textsubscript{2}, MgZn\textsubscript{2}, and MgNi\textsubscript{2}) and a [CaCu\textsubscript{5}] type structure. From what is known of the hydrogen storage properties of LaNi\textsubscript{5} and YNi\textsubscript{2}, the possibility of a new ternary Ln\textsubscript{2}Ni\textsubscript{5} (Ln = La, Ce) system alloy has been studied as a negative electrode material for Ni–MH batteries.\textsuperscript{14} This compound has the same PuNi\textsubscript{3}-type structure as that of LaMg\textsubscript{2}Ni\textsubscript{5}. Synthesis of MgYNi\textsubscript{4}\textsuperscript{15} has, in addition, been reported with respect to the R–Mg–Ni system.

We analyzed the crystal structures of the unknown phases\textsuperscript{16} in La–Mg–Ni–Co system alloys in which Co partly replaces Ni or forms solid solution. Here we report our discovery of the existence of more than three new kinds of phase. We show that the layered structure model proposed thus far\textsuperscript{8,9} can also be applied to the La–Mg–Ni system, and that this alloy system has the ability to form a material group with versatile layered structures.

2. Experimental Method

Alloy samples were prepared by mixing each metallic element in a predetermined elemental ratio and by melting them in a HF melting furnace in an argon atmosphere. The samples were then annealed for 5 h at 900–1000°C. Two kinds of alloy composition were prepared, i.e., La\textsubscript{2}Mg\textsubscript{2}Ni\textsubscript{5} and La\textsubscript{2}Mg\textsubscript{2}Ni\textsubscript{5}Co\textsubscript{0.5}; these ingots are hereafter called alloys T1 and T2, respectively.

Compositional analysis of the alloys was performed using an inductively coupled plasma spectrometer (ICP) (Model IRIS/AP; Thermo Jarrel Ash Instruments, USA). Quantitative analysis of the elements La, Mg, Ni, Co, and Al was carried out. Samples were dissolved in 1+1 HCl, and the solution was then diluted to prepare samples for analysis.

Local compositional analysis of the alloys and of the crystals used in a single crystal analysis was carried out using a scanning electron microscope (SEM; Model S-2350, Hitachi Ltd) combined with an energy dispersive X-ray spectrometer (EDX; Model EMAX-2770, Horiba Ltd).

The alloy phases were identified by using a powder X-ray diffractometer (XRD; Model RAX-01, Rigaku Corp.). We used a Cu-Kα radiation monochromatized with a curved graphite monochromator, and measurements were made at 40 kV–40 mA. Ordinary data for the Rietveld analysis were collected by a step-scan method (measurement conditions: 2θ = 15–140°, 10 s/step, and 0.02°/step). Because we expected a c-axis long-period structure in these alloys, the low angle range, 2θ = 3–20°, was meticulously measured, taking a long time (100 s/step, and 0.02°/step) by the step-scan method. The software used in the analysis was XPRESS (MAC Science Co. Ltd.) The Rietveld analysis program used was RIETAN2000.\textsuperscript{17}

Precession photographs were taken with a Burger precession camera (Rigaku) (Mo-Kα radiation, 40 kV–20 mA). Portions of the T1 and the T2 ingots were lightly crushed. Crystals that showed the cleavage faces commonly observed in single crystals were then picked up and used in taking the precession photographs. Three kinds of single crystal (T1-A, T1-B, and T2-B), which were judged to be good crystals and regarded as having different structures from those in the precession photographs, were used in measuring the diffraction intensities. The four-circle single crystal intensity measurement apparatus used was a Rotorflex Model RA-SA-7R (Rigaku). The measurement conditions were: Mo-Kα radiation, 50 kV and 200 mA. The diffraction intensity was measured by the o-scan method. Absorption correction was made by the ψ-scan method. The shapes and dimensions of the single crystals used in the measurements were: T1-A: tabular crystal, 150 × 150 × 25 μm; T1-B: columnar crystal, 50 × 60 × 210 μm; T2-B: blocky crystal, 135 × 160 × 200 μm. The software used was the crystal structure analysis package “teXsan” 1.11.

3. Results and Discussion

3.1 Alloy compositions and identification of phases by X-ray diffraction

Table 1 compares the predetermined compositions of the alloys and the results of ICP and EDX analyses of the prepared alloys. Alloy T1 was prepared with a composition close to the predetermined one. In the synthesized alloy T2, on the other hand, the Mg content was a little lower than the predetermined content, and there was also a trace amount of Al. We deduced that the Al had been mixed in from an alumina crucible, because alloy T2 had to be melted at a higher temperature than did alloy T1. Both alloys had 4 primary constituent elements—La, Mg, Ni, and Co—and the proportions of these elements were confirmed to be close to the predetermined ones.

The XRD pattern of alloy T1 is shown in Fig. 2. The XRD pattern of this alloy was complex and included many small peaks. Figure 2 also shows the magnified XRD pattern obtained by step-scanning with a long exposure (100 s/step) in the low angle range. Extremely weak peaks with d(θ) = 0.819, and 0.609 nm are apparent. This pattern suggested a superlattice structure with AB\textsubscript{5}, LaNi\textsubscript{3}, and MgNi\textsubscript{2} structures. From what is known of the hydrogen storage properties of LaNi\textsubscript{5} and YNi\textsubscript{2}, the possibility of a new ternary Ln\textsubscript{2}Ni\textsubscript{5} (Ln = La, Ce) system

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>Unit Cell Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi\textsubscript{3}</td>
<td>a = 1.62 nm, b = 1.62 nm, c = 1.80 nm</td>
</tr>
<tr>
<td>MgNi\textsubscript{2}</td>
<td>a = 0.819 nm, b = 0.609 nm</td>
</tr>
<tr>
<td>AB\textsubscript{5}</td>
<td>a = 0.819 nm, b = 0.609 nm</td>
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</table>

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>SPACE Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi\textsubscript{3}</td>
<td>Fm-3m</td>
</tr>
<tr>
<td>MgNi\textsubscript{2}</td>
<td>I4/mmm</td>
</tr>
<tr>
<td>AB\textsubscript{5}</td>
<td>P6\textsubscript{3}m</td>
</tr>
</tbody>
</table>

The XRD pattern of alloy T2 is shown in Fig. 3. The XRD pattern of this alloy also included many small peaks, similar to those observed in Fig. 2, and was quite complex. Figure 3 also shows the magnified XRD pattern obtained by step-scanning with a 100 s/step in the low angle range (as in
Table 1 Chemical composition analyses of La-Mg-Ni-Co alloys. The number in a parenthesis shows standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>La (mass%)</th>
<th>Mg (mass%)</th>
<th>Ni (mass%)</th>
<th>Co (mass%)</th>
<th>Al (mass%)</th>
<th>sum (mass%)</th>
<th>Composition*</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1 sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starting composition</td>
<td>34.64</td>
<td>2.60</td>
<td>52.26</td>
<td>10.30</td>
<td>0.00</td>
<td>100.00</td>
<td>La$<em>{0.75}$Mg$</em>{0.25}$Ni$<em>3$Co$</em>{0.50}$</td>
</tr>
<tr>
<td>ICP analysis</td>
<td>(0.4)</td>
<td>(0.1)</td>
<td>(0.6)</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>99.3</td>
<td>La$<em>{0.70}$Mg$</em>{0.30}$Ni$<em>{2.40}$Co$</em>{0.50}$</td>
</tr>
<tr>
<td>EDX analysis</td>
<td>(0.5)</td>
<td>(0.2)</td>
<td>(0.6)</td>
<td>(0.2)</td>
<td>(0.2)</td>
<td>100.0</td>
<td>La$<em>{0.71}$Mg$</em>{0.21}$Ni$<em>{2.50}$Co$</em>{0.49}$</td>
</tr>
<tr>
<td>T2 sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starting composition</td>
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<td>2.30</td>
<td>55.54</td>
<td>9.30</td>
<td>0.00</td>
<td>100.00</td>
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</tr>
<tr>
<td>ICP analysis</td>
<td>(0.3)</td>
<td>(0.1)</td>
<td>(0.7)</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>99.3</td>
<td>La$<em>{0.76}$Mg$</em>{0.25}$Ni$<em>{3.30}$Co$</em>{0.40}$</td>
</tr>
<tr>
<td>EDX analysis</td>
<td>(0.5)</td>
<td>(0.2)</td>
<td>(0.6)</td>
<td>(0.3)</td>
<td>(0.2)</td>
<td>100.0</td>
<td>La$<em>{0.81}$Mg$</em>{0.15}$Ni$<em>{3.30}$Co$</em>{0.40}$</td>
</tr>
</tbody>
</table>

*) Upper row in composition: La + Mg = 1.00, Lower row: Ni + Co = 3.00 (in parenthesis)

Fig. 2 X-ray diffraction profile of T1 sample.

Fig. 3 X-ray diffraction profile of T2 sample.

Five weak long-period peaks are apparent in the low angle range, $2\theta < 20$. When we attempted to index these peaks, we deduced that they were attributed to a mixed phase composed of at least two phases with $c$-axis periods of 2.44 nm (T2-A phase) and 3.23 nm (T2-B phase).

As described above, both alloys T1 and T2 had complex XRD patterns suggesting long-period structures, in which all peaks were unable to be indexed by a single set of lattice constants. Microscopic observation of the alloy surfaces showed dark and light portions, indicating inhomogeneous alloys.

3.2 Crystal structures of La–Mg–Ni–Co system alloys

Accordingly, after the alloys had been roughly crushed, we picked up those crystals that showed mirror-like facets as close to those of single crystals as possible under a stereoscopic microscope, and we then took precession photographs. We determined the crystal orientations by eliminating unnecessary crystals, and we obtained precession photographs showing clear diffraction spots very close to those of single crystals. From these photographs, we found 2 kinds of structure for each alloy and 3 different structures altogether. Table 2 summarizes the results of our EDX analyses of their composition, and Table 3 summarizes the crystallographic data.

3.2.1 Structure of T1-A alloy

Crystals that showed tabular cleavage were present in alloys T1 and T2. The crystallographic data obtained from the precession photographs of the tabular crystals showed that their crystal systems were hexagonal, and their lattice constants were $a = 0.504\, \text{nm}$, $c = 2.42\, \text{nm}$, and $c/a = 4.80$. These data are equivalent to those of the A-phase with $c = 2.44\, \text{nm}$ that exists in the XRD patterns shown in Figs. 2 and 3. This lattice had a long-period structure close to the lattice of LaNi$_5$ (hexagonal, P6/mmc, $a_0 = 0.5017\, \text{nm}$, $c_0 = 0.3987\, \text{nm}$) with an approximately 6-time elongated $c$-axis, and was characterized by strong diffraction spots with a 6-time period in the $c^*$ orientation. Because pseudo-extinction rule, $l = 2n + 1$ in (000l) and $l = 2n + 1$ in ($h$2$h$0) are recognized and a possible space group is P6$_3$/mmc (No. 194), P6$_5$mc (No. 186), or P62c (No. 190). We found that the crystallographic data for this lattice were extremely close to those of La$_2$Ni$_7$ (hexagonal, P6$_3$/mmc, $a = 0.5053\, \text{nm}$, and $c = 2.462\, \text{nm})$ with a Ce$_2$Ni$_5$-type structure. This phase is called T1-A (or T2-A) hereafter.
The existence of two types of polytype transformations—Ce₂Ni₇ and Gd₂Co₃ types—is known with regard to La₇Ni₇ composition,¹⁹ and it has been reported that the La₂Ni₇ 2H transformation is stable up to the melting point, and that the 3R transformation does not exist.²³ Buschow et al.²⁰ discussed the stability of R₂Ni₇ transformation and found it to be dependent on the atomic radius of the rare earth element R; that is, a 2H structure develops with a larger atomic radius and a 3R structure with a smaller atomic radius. This crystal had an approximately 1.5% shorter c-axis than the La₇Ni₇ with a Ce₂Ni₇-type structure. Therefore, we deduced that the La site was either dissolved or replaced by Mg with a smaller atomic radius, and the crystal had a 2H structure.

The T1-A crystal was measured by a four-circle single crystal diffractometer. This was not necessarily a good single crystal appropriate for single crystal analysis, because it had many trivial weak diffraction spots, split profiles, and asymmetrical background (BG) peaks. As the result of refinement of the lattice constants using 23 strong peaks as asymmetrical background (BG) peaks, as the result of many trivial weak diffraction spots, split profiles, and crystal appropriate for single crystal analysis, because it had a hexagonal lattice with a 2H structure. This was not necessarily a good single crystal suitable for detailed structural refinement, further analysis was difficult.

This structure has, when described by its La₂Ni₇ composition, two blocks forming one period and cyclically stacked with a 60° rotation along the c-axis, each block being composed of one Laves-structure [La₂Ni₄] layer and two CaCu₅-type [La₇Ni₁₃] layers. It can be classified as a 2H-type structure by the Ramsdell notation.²¹ In the most appropriate structure deduced from the above results, Mg is dissolved at the La site of the Laves-structure [La₂Ni₄] layer, which has an La–La interatomic distance as short as 0.32 nm, and not in the [CaCu₅]-type [La₇Ni₁₃] layer, which has an La–La interatomic distance not shorter than 0.38 nm. The La sites in the Laves layer of the T1-A composition were occupied by La and Mg in a ratio of approximately 1:1. Assuming a structure in which the Laves layers were occupied by La and Mg in a ratio of 1:1, the crystal can be described as a compound with the stoichiometric composition La₃MgNi₁₄, proposed by Kohno et al.¹ However, when assuming the space group of P6/mmmc, it can be described as an Mg-dissolved alloy with a crystallographic composition formula of (La₂-.₃Mg)La₂Ni₁₄, because the sites of La and Mg are equivalent in the Laves layer. According to the results of our EDX analysis of the T1-A crystal (Table 2), its composition is [La₀.₈₀Mg₀.₂₁Ni₂.₉₄Co₀.₅₅]. From the EDX analysis results, x = 0.84 is obtained, indicating that slightly more La is included than Mg. By refining the occupancy ratio using the X-ray intensity data of the single crystal, we obtained x = 0.90(2), which almost agrees with the above result. Although both the EDX analysis and the single crystal analysis results show that Mg is slightly lacking, the composition agrees with the stoichiometric composition, La₃MgNi₁₄, proposed by Kohno et al.¹ considering the precision of the data and the EDX analysis results for the

<table>
<thead>
<tr>
<th>Crystal No.</th>
<th>T1-A, T2-A</th>
<th>T1-B</th>
<th>T2-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>La₃Mg(Ni, Co)₁₄</td>
<td>La₃Mg(Ni, Co)₉</td>
<td>La₃Mg(Ni, Co)₁₉</td>
</tr>
<tr>
<td>Structure type</td>
<td>Ce₂Ni₇</td>
<td>P₆₃/mmc</td>
<td>P₆₃/mmc</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>1263.29</td>
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<td>1695.85</td>
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<tr>
<td>Crystal system</td>
<td>Hexagonal</td>
<td>Trigonal</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Space group</td>
<td>P₆₃/mmc</td>
<td>R₃m</td>
<td>P₆₃/mmc</td>
</tr>
<tr>
<td>Cell dimension</td>
<td>a/Å</td>
<td>0.5052(1)</td>
<td>0.5052(1)</td>
</tr>
<tr>
<td></td>
<td>c/Å</td>
<td>2.4245(3)</td>
<td>2.4200(2)</td>
</tr>
<tr>
<td>Volume</td>
<td>V/Å³</td>
<td>0.5358(3)</td>
<td>0.5436(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Density</td>
<td>D/Å²/Mg/cm³</td>
<td>7.83</td>
<td>7.61</td>
</tr>
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</table>
in the T1-A crystal; therefore, the possible space group was deduced from the extinction rule was different from that of T1-A. We essentially recognized an extinction rule of \(-h + k + l = 3n\) in \((h k l)\), which is peculiar to the rhombohedral crystal with hexagonal lattice axes. Diffraction conditions were observed under which diffractions for other than \(l = 3n\) in \((00l)\) disappeared; therefore, the possible space group deduced from the extinction rule was R32 (No. 155), R3m (No. 160), or R3\(\overline{m}\) (No. 166). However, in the precession photograph we also observed (200) diffraction spots, though they were weak, violating the extinction rule. It was assumed that they were diffraction spots from another crystal, because the crystal was picked up from the crushed ingot and was therefore not good for analysis. If this was not the case, there was a possibility of lower symmetry than those of the above space groups. Many trivial weak diffraction spots and asymmetrical BG peaks were found in the four-cycle single crystal diffractometer, as in the T1-A crystal; therefore, again, the crystal was not necessarily ideal for single crystal analysis. The lattice constants were refined as \(a = 0.5062(1)\) and \(c = 2.4500(2)\) nm with a hexagonal lattice axis (Table 3). The long period (c-axis) of this phase agreed with that of the B-phase with \(2.45\) nm found in the XRD pattern shown in Fig. 2. Hereafter we call this crystal the T1-B crystal.

The T1-B crystal was similar to the PuNi\(_3\)-type structure LaNi\(_3\) (R3m, \(a = 0.5086\) nm, and \(c = 2.501(1)\) nm).\(^{19}\) Its structure was different from that of the 2H-type hexagonal CeNi\(_3\)\(^{23}\) which is the other polytype with the same stoichiometric composition. Kadir et al. have synthesized a new ternary RMg\(_2\)Ni\(_3\) \((R = \text{La, Ce, Pr, Nd, Sm, or Gd})\) with a PuNi\(_3\) structure, and have refined their structures by the Rietveld method.\(^{10}\) Although the T1-B crystal had a structure similar to that of the said alloy, its Mg content was greatly different from that of this alloy. From the results of our EDX analysis (Table 2) of the single crystal, the composition of the T1-B crystal was determined to be \([\text{La}_{0.70}\text{Mg}_{0.15}\text{Ni}_{2.53}\text{Co}_{0.7}]\) on the basis of the atomic ratio Ni + Co = 3.0. This formula shows that La + Mg = 0.85, assuming that La and Mg are dissolved, leading to the composition \(\text{La}_{0.70}\text{Mg}_{0.15}\text{Ni}_{2.53}\text{Co}_{0.7}\) \((x = 0.5)\) which lacks approximately half of Mg. When we assumed that the crystal had a PuNi\(_3\)-structure \((\text{La}_{2-}\text{Mg}.)\) composition, \(x = 0.45\) was obtained from the EDX and \(x = 0.44\) from the single crystal analysis, values that were almost the same. Although the lattice constants of the T1-B crystal were approximately 2.6% larger than those of La\(_{0.70}\text{Mg}_{0.15}\text{Ni}_{2.53}\text{Co}_{0.7}\) \((a = 0.49241\) nm, and \(c = 2.3875(1)\) nm),\(^{13}\) their axial ratios were the same, i.e. \(c/a = 4.85\). We assumed that the difference in the sizes of the lattices was caused mainly by a difference in the composition ratios of La \((r = 0.1877\) nm) with a larger metal radius and Mg \((r = 0.1602\) nm) with a smaller metal radius.\(^{23}\)

The basic structure of the T1-B crystal was three units stacked along the c-axis direction, with each unit misaligned by 1/3 in the [120] direction, forming one period and returning to the original position. Each unit was a block of stacked layers composed of one [CaCu\(_3\)]-type layer and one Laves-phase [MgZn\(_2\)] layer. In the LaMg\(_2\)Ni\(_3\) structure reported by Kadir et al., the 6c site of the Laves-structure portion is completely occupied by Mg. We consider that the T1-B crystal was different from that of LaMg\(_2\)Ni\(_3\) reported by Kadir et al., because the interatomic distance between the 6c sites of the T1-B crystal was 0.32\(\) nm, which is too long for an Mg–Mg distance. Therefore, we can visualize a solid solution of La and Mg and the presence of an ordered structure at the site due to less symmetry or deficiency. A solid solution structural model for PuNi\(_3\) (space group: R\(3\)m), in which the 6c site of the Laves-structure portion was dissolved by La and Mg, gave a very poor R value \((R = 29%)\) in the single crystal structure analysis. However, in the chemical formula La\((\text{La}_{2-}\text{Mg}_{0.7}\text{Ni}_{0.3})\text{Co}_{0.7}\) which has a structure similar to that of PuNi\(_3\), the solid solution amount is estimated to be \(x = 0.4–1.0\); therefore, the ideal composition formula deduced from the structure agreed with that of the stoichiometric composition alloy La\(_2\)MgNi\(_3\), proposed by Kohno et al.\(^{11}\)

The finding of two kinds of structure—T1-A and T1-B crystals—in alloy T1 agreed with the XRD pattern in Fig. 2. The results of XRD pattern identification by the Rietveld analysis are explained later in this report.

### 3.2.3 Structure of the T2-B crystal

Two kinds of crystal were also present in alloy T2. From the precession photographs, one of them was found to have the same crystal system as that of the T1-A crystal (T2-A). The other was a crystal of a rectangular-parallelepiped shape, which was hexagonal and had lattice constants with a still longer c-axis period, \(a = 0.502\) nm, \(c = 3.21\) nm, and \(c/a = 6.39\). It had a long-period structure with a c-axis period still longer than those of the crystals described so far. Although the \((hk0)\) photograph shows very clear diffraction spots, streaks are apparent, indicating the presence of lattice defects. Diffraction spots in the c*-orientation were characterized by the presence of strong spots at an 8-time period. The spacing was close to 8 times the c-axis of LaNi\(_3\). The a-axes of T1-A, -B, and LaNi\(_3\) related to this crystal were approximately the same (approximately 0.5\(\) nm).

The possible extinction rules of this crystal were \(l = 2n + 1\) in \((00l)\) and \(l = 2n + 1\) in \((hh2h)\). From these results, the possible space group was P\(\overline{6}m)(194), P\(\overline{6}m\)c (186), or P\(6\)c (190). We performed a four-cycle X-ray intensity measurement using a blocky crystal \((135 \times 160 \times 200\mu\text{m})\). We found that this crystal was not a good single crystal because it had many trivial weak diffraction spots, split profiles, and asymmetrical BG peaks, as did the two crystals described above. The lattice constants were refined to \(a = 0.5042(2)\) nm and \(c = 3.2232(3)\) nm. This crystal is called the T2-B crystal hereafter.

According to the results of our EDX compositional analysis (Table 2), the composition of the T2-B single crystal was La\(_{0.80}\)Mg\(_{0.20}\)Ni\(_{3.56}\)Co\(_{0.55}\), on the basis of \(\text{La} + \text{Mg} = 1.0\). This formula is close to La\(_3\)Ni\(_9\), assuming that La and Mg, and Ni and Co, are respectively dissolved at the
same sites. It can also be expressed by \( \text{La}_8\text{Mg}_{0.19}\text{Ni}_{1.27}\text{Co}_{0.53} \) if we set \( \text{Ni} + \text{Co} = 3.8 \), which is a composition slightly lacking in \( \text{La} + \text{Mg} \).

The \( \text{La}_8\text{Ni}_{19} \) phase has been reported to be a high temperature phase stable at and above 900 °C and up to 1014 °C, as shown in the \( \text{La}-\text{Ni} \) system phase diagram (Fig. 1). It has a rhombohedral structure (\( \text{Ce}_2\text{Co}_{19} \)-type structure, space group: \( \text{R}3\text{m} \)) expressed as a \( 3\text{R} \)-type by the Ramsdell notation, and does not have a \( 2\text{H} \)-type hexagonal structure. However, the \( \text{T}_2 \)-\( \text{B} \) crystal that we analyzed did have a \( 2\text{H} \) structure, contrary to the concept of Buschow et al. with regard to the stability of \( \text{R}_2\text{Ni}_7 \) transformations.

Because the \( \text{La}_8\text{Ni}_{19} \) structure existed stably as a main phase even after the \( \text{T}_2 \)-\( \text{B} \) crystal had been additionally annealed for 1 week at 800 °C and furnace-cooled, we consider that it could exist stably down to low temperatures without being strained, thanks to the inclusion of Mg. This structure had the same crystallographic data as those of the \( 2\text{H} \) type (space group: \( \text{P}6_3/\text{mmc} \)) \( \text{Pr}_3\text{Co}_{19} \) (Card Number 42–1198 of the JCPDS database for powder diffraction data). Here we call this structure a \( \text{Pr}_3\text{Co}_{19} \)-type structure.

In our structural analysis of the \( \text{T}_2 \)-\( \text{B} \) single crystal, identification of the basic structure of the crystal was refined to that of a \( \text{Pr}_3\text{Co}_{19} \) type (\( \text{P}6_3/\text{mmc} \)). That is to say, it had a \( 2\text{H} \) structure with a \( \text{La}_8\text{Ni}_{19} \) composition. It had a layered structure with the \( c \)-axis at 3.2 nm, forming one period with two blocks stacked with a 60° rotation, each block being composed of one \( \text{Laves} [\text{MgZn}_2] \)-type [\( \text{La}_2\text{Ni}_4 \)] layer and three \( [\text{CaCu}_3] \)-type \( [\text{LaNi}_3] \) layers. The results of our single crystal structure analysis revealed that the \( \text{T}_2 \)-\( \text{B} \) crystal had Mg solubility of approximately 50% at the \( \text{La} \) site of the \( [\text{La}_2\text{Ni}_4] \) layer. Because the distance between \( \text{La} \) sites was shorter (0.32 nm) in the \( [\text{La}_2\text{Ni}_4] \) layer than in the \( [\text{LaNi}_3] \) layer (0.39 nm), the above is an appropriate result considering the difference in metal radii of \( \text{La} \) and Mg. However, the \( R \) values were \( R = 10.5% \) and \( R_p = 17.7% \) when an isotropic temperature factor was incorporated into the refined analysis.

The composition of the \( \text{T}_2 \)-\( \text{B} \) crystal, from the single crystal structure analysis, can be described by \( (\text{La}_2\text{Mg}_{x}\text{Ni}_{14})(\text{LaNi}_3) \) \( (x = 1.0) \), in which half of the \( \text{La} \) sites in the \( \text{Laves} \) \( [\text{La}_2\text{Ni}_4] \) layer are occupied by Mg. The crystal’s stoichiometric composition can be described by \( \text{La}_4\text{MgNi}_{10} \). It was possible that \( \text{La} \) and Mg were ordered, since the numbers of these atoms were the same in the \( [\text{La}_2\text{Ni}_4] \) layer of the \( \text{T}_2 \)-\( \text{B} \) crystal. However, the most appropriate result was that half of the \( \text{La} \) sites in the \( \text{Laves} \)-type layer were dissolved by Mg, as in the structural analyses of the \( \text{T}_1 \)-\( \text{A} \) and \( \text{-B} \) crystals, considering the reliability factors and the interatomic distance between the \( \text{La} \) sites. A more detailed structural analysis of the single crystal is currently in progress.

### 3.3 Identification of alloy phases by Rietveld analysis

Phase identification of alloys \( \text{T}_1 \) and \( \text{T}_2 \) was conducted by Rietveld analysis on the basis of the above-described experimental results.

The results of the Rietveld analysis of alloy \( \text{T}_1 \) are shown in Fig. 4. In addition to the \( \text{PuNi}_3 \)-type \( \text{La}_2\text{MgNi}_6 \) and \( \text{Ce}_2\text{Ni}_7 \)-type \( \text{La}_4\text{MgNi}_{14} \) phases confirmed by the single crystal analysis, a \( \text{2H-Pr}_3\text{Co}_{19} \)-type \( \text{La}_4\text{MgNi}_{19} \) phase and a \( \text{C15b} \)-type \( \text{LaMgNi}_{14} \) phase were marginally identified. The ratios of these phases were 51%, 25%, 15%, and 9%, respectively: approximately half was the \( \text{PuNi}_3 \)-type phase. Lattice constants were \( a = 0.50559(4) \) nm and \( c = 2.4486(2) \) nm for the \( \text{PuNi}_3 \) phase; \( a = 0.50496(6) \) nm and \( c = 2.4302(2) \) nm for the \( \text{Ce}_2\text{Ni}_7 \)-type phase; and \( a = 0.5049(1) \) nm and \( c = 3.2251(4) \) nm for the \( \text{Pr}_3\text{Co}_{19} \) phase, which were almost the same as those obtained with the single crystals (Table 3). The \( c \)-axis of the \( \text{Ce}_2\text{Ni}_7 \)-type phase was slightly (0.2%) longer; this might be a result of either strong interaction caused by the similarity of its lattice constants with those of the \( \text{PuNi}_3 \)-type phase, or heterogeneity of the sample.

When the XRD pattern of alloy \( \text{T}_1 \) was refined using the three-phase mixture of \( \text{PuNi}_3 \)-type + \( \text{Ce}_2\text{Ni}_7 \)-type + \( \text{Pr}_3\text{Co}_{19} \)-type phases, the \( R \) values were poor \( (R_p = 12.8% \) and \( R_p = 10.0% \) after eliminating a certain number of impurity peaks, and a small number of diffraction peaks were left unidentified. The 003 peak \( (d = 0.8185 \) nm) shown in the magnified diagram for the low angle range in Fig. 2 was similar to the peak equivalent to index 002 of the \( \text{CeNi}_3 \)-type structure. However, the strong peak for index 105 characteristic of the \( \text{CeNi}_3 \)-type structure was not observed at around \( 2\theta = 34.2° \), and refinement was not achieved in the Rietveld analysis incorporating the \( \text{CeNi}_3 \)-type structure. Consequently, it was concluded that the \( \text{CeNi}_3 \)-type structure phase did not exist in this XRD pattern. The unknown diffraction peak at \( 2\theta = 24.7° \) was similar to the appearance pattern of index 004 of \( \text{LaMg}_2\text{Ni}_9 \) and \( (\text{La}_{0.65}\text{Cu}_{0.35})(\text{Mg}_{0.12}\text{Ca}_{0.68})\text{Ni}_{10} ) \). In the model simulation of the \( \text{La} \) solid–solution in the Mg site, the diffraction peak with index 104 showed a tendency to become stronger with increasing Mg occupancy ratio of the 6c sites. In the Rietveld analysis, however, we were unable to identify this diffraction peak as the diffraction peak of the \( \text{PuNi}_3 \)-type phase with a composition similar to that of \( \text{LaMg}_2\text{Ni}_9 \), in light of its consistency with other diffraction patterns. When we attempted to match the diffraction peak at \( 2\theta = 24.7° \), contradictions occurred also in the lattice constants and with the difference in atomic radii of \( \text{La} \) and Mg. Unidentified residual peaks were also observed at around \( 2\theta = 63.3, 67.5, \) and \( 74.6° \). These residual peaks were found...
to be similar to those of a C15b-type MgYNi4 structure (space group: F43m),\textsuperscript{15} not to those of a cubic C15-type La1−xMg2xNi2 phase. The unidentified peak at 2θ = 24.7° agreed with the (200) peak, and this can be considered proof of the ordering of La and Mg. The lattice constant was refined to 0.7191(1) nm. As a result of refinement with the 4 phases, very good agreement was obtained (Fig. 4). The reliability factors finally obtained were \( R_{wp} = 7.96\% \), \( R_p = 6.09\% \), \( R_e = 4.86\% \), and \( S = 1.638 \).

However, this system can have various combinations of stacking patterns, as can be seen in the layered structure models shown in the next section. From TEM observations, one of the current authors has suggested the existence of a new hybrid block structure phase and of a CeNi3-type phase.\textsuperscript{11} Various phenomena of different stacking patterns have been observed in TEM observations,\textsuperscript{25} and therefore, various phenomena might be related to stacking faults or stacking irregulars.

The final atomic coordinates of the Ce2Ni7-type La4MgNi19 and the PuNi1-type La3MgNi18 of the T1 sample, as refined by the Rietveld analysis, are shown in Tables 4 and 5, respectively.

The final result of the Rietveld analysis of sample T2 is shown in Fig. 5. The main phases identified were the 2H-type La2MgNi19 and the Ce2Ni-type La3MgNi14, which were found by the single crystal analysis. Trace amounts of a CaCu5-type LaNi5 and 3R-type La3MgNi19 were also identified. Lattice constants of the main phases were \( a = 0.50403(3) \text{ nm} \) and \( c = 3.2232(2) \text{ nm} \) for the 2H-type La2MgNi19, and \( a = 0.50422(5) \text{ nm} \) and \( c = 2.4265(3) \text{ nm} \) for the Ce2Ni-type La3MgNi14. These values agree with those in Table 3 obtained with the single crystal. The first refinement with a three-phase mixture gave \( R_{wp} = 12.3\% \), and left a small number of unidentified peaks (a peak at 2θ = 31.3° in Fig. 5, for example), suggesting the existence of an unknown phase(s). These unidentified peaks were later found to be similar to those of the 3R-type Ce3Co9-structure La2MgNi19 (lattice constants: \( a = 0.5070(1) \text{ nm} \), \( c = 4.877(1) \text{ nm} \)). Because its existence ratio was as small as 3%, a detailed analysis was prevented. However, the R-values were slightly improved (\( R_p = 11.7\% \), \( R_e = 9.4\% \), \( R_e = 5.0\% \), \( S = 2.32 \)). The ratios of each phase (2H-La4MgNi19, 2H-La3MgNi14, LaNi5, and 3R-La3MgNi19) were 62\%, 29\%, 6\%, and 3\%, respectively. The refined atomic coordinates of the 2H-type La4MgNi19 of the T2 sample determined by the Rietveld analysis are shown in Table 6.

We studied the interatomic distances derived from the atomic coordinates refined by the Rietveld analysis. Of all the structures of these three main phases, the La–La distance in the [CaCu5] layer was not shorter than 0.38 nm, which was in the normal range, and that in the [MgZn2] layers was as short as 0.32 nm. The interatomic distance of the La–La atoms bridging the [CaCu5] and [MgZn2] layers was 0.35 nm, which was about the above two numbers. This result indicates that Mg selectively occupies the La site and relieves strain on the [MgZn2] layer, thus contributing to the formation of a stable structure.

### 3.4 Layered structure models for the La–Mg–Ni system

Figure 6 shows layered structural models for the La–Mg–Ni system alloys. These layered structure models were made with reference to reports by Komura\textsuperscript{39} and Yamamoto \textit{et al.}\textsuperscript{41}

Various layered structural models can be conceived, with a basic unit stacked with the Laves-type [La2Ni12] and the CaCu5-type [LaNi5] layers.

[3C-type]: LaMgNi14, PuNi1-type (3R-type) La3MgNi5, and Ce2Ni-type (2H-type) La3MgNi14 phases were found in alloy T1, and Ce2Ni5-type (2H-type) La3MgNi14, Pr5Co9-type (2H-type) La12MgNi19, and Cu4Co-type LaNi5 phases were found in alloy T2. They correspond to (a), (c), (d), (f), and (h) in Fig. 6.
Table 6 Refined atomic fractional coordinates, isotropic thermal displacements and occupation numbers of La$_x$Mg$_{1-x}$Ni$_{4}$ obtained from the powder X-ray Rietveld analysis of T2 alloy. Pr$_{5}$Co$_{10}$-type, Space group P6$_3$/mmc, $a = 0.5040(3)$ nm, $c = 3.2232(2)$ nm.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$g$</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>B $(10^2$/nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(1)</td>
<td>2c</td>
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<td>1/3</td>
<td>2/3</td>
<td>1/4</td>
<td>1.7(2)</td>
</tr>
<tr>
<td>La(2)</td>
<td>4f</td>
<td>1.0</td>
<td>1/3</td>
<td>2/3</td>
<td>0.1280(1)</td>
<td>1.4(1)</td>
</tr>
<tr>
<td>La/Mg(3)</td>
<td>4f</td>
<td>0.5(0.5)</td>
<td>1/3</td>
<td>2/3</td>
<td>0.0193(2)</td>
<td>1.2(2)</td>
</tr>
<tr>
<td>Ni/Co(1)</td>
<td>2a</td>
<td>0.86/0.14</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.4(1)</td>
</tr>
<tr>
<td>Ni/Co(2)</td>
<td>2b</td>
<td>0.86/0.14</td>
<td>0.0</td>
<td>0.0</td>
<td>1/4</td>
<td>0.4</td>
</tr>
<tr>
<td>Ni/Co(3)</td>
<td>2d</td>
<td>0.86/0.14</td>
<td>2/3</td>
<td>1/3</td>
<td>1/4</td>
<td>0.4</td>
</tr>
<tr>
<td>Ni/Co(4)</td>
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<td>0.0</td>
<td>0.1261(2)</td>
<td>0.4</td>
</tr>
<tr>
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<td>1/3</td>
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<td>2x</td>
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<td>0.1658(7)</td>
<td>2x</td>
<td>-0.1888(2)</td>
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</tr>
</tbody>
</table>

Fig. 6 Schematic representation of the structure stacking model$^{13}$ for La–Mg–Ni system.

A trace of (g) was also found. All of these structures are basically explained by differences in the pattern by which (a) the Laves-type [LaMgNi$_4$] layer and (b) the CaCu$_5$-type [LaNi$_5$] layer are stacked along the c-axis. All of the Mg either replaced approximately 50% of the La sites or was dissolved in such sites in the Laves-type [LaNi$_5$] layer. Neither replacement nor solid solution by Mg in the [LaNi$_5$] layer was observed.

The general formula for this series of compounds can be expressed by [LaMgNi$_{4-n}$]$_n$[LaNi$_{5}$]$_n$, i.e., La$_{4n+1}$MgNi$_{5n+4}$, using Khan’s expression for the general formula, LaNi$_5$ with $x = (5n + 4)/(n + 2)$, where $n$ is the number of LaNi$_5$ layers in the block.$^{39}$

From our preliminary structural analysis of single crystals, a solid–solution structure is possible, because La and Mg in the Laves layer are positioned in the equivalent sites in the P6$_3$/mmc space group. Although both Ce$_2$Ni$_7$-type and Pr$_5$Co$_{10}$-type structures belong to the P6$_3$/mmc space group, the atomic ratio of La to Mg was almost 1:1 in the Laves layer in the current study, and they behaved as if they were ordered. If the structure is a dissolved one, then the Mg solid–solution range might be narrow. If La and Mg in the Laves layer form solid solution, then the general formula can be expressed by [La$_{4-n}$Mg$_n$Ni$_{5n}$]$_n$[LaNi$_5$], i.e., La$_{4n+1}$Mg$_n$Ni$_{5n+4}$ ($x$ is the Mg ratio in the Laves phase). The general formula can also be expressed by La$_{4n+1}$Mg$_n$Ni$_{5n+4}$ for m layers of the Laves layers by stretching the expression.

Numerous polytypes (2H, 3R, 4H, 5T, 6H, 7R, 9R, 12R, 15R, etc.) by the Rietveld notation$^{31}$ have been found in Sm$_2$Ni$_3$ and Sm$_2$Ni$_5$ by electron microscopy and electron diffraction.$^{3,20}$ Polytype transformations that can be expressed by 2H, 3R, etc., were found in the bulk samples of each composition of this La–Mg–Ni system, and, therefore, many more of them might exist.

Furthermore, Kohno et al.$^{1}$ under TEM, have observed a structure with a 2.05 nm stacking period, and have proposed the existence of La$_3$MgNi$_2$3 with a hybrid layered structure that is intermediate between those of La$_2$MgNi$_9$ and La$_3$MgNi$_{14}$. However, the existence of such a phase was not confirmed in our crystallographic study of bulk samples of the current alloy systems.

The La–Mg–Ni system, as has been reported by Kohno et al.$^{1}$ from the results of TEM observations, is characterized by the formation of a layered structure composed of AB$_5$ and AB$_2$ units. From the Rietveld analysis of powder X-ray diffraction, both alloys T1 and T2 were found to be ones in which the abovementioned structure phases with different stacking patterns coexisted as the main phases. However, because the existence of unidentified phases has been suggested, and because the existence of numerous phases with various combinations of AB$_5$ and AB$_2$ units can be conceived, this alloy system can most likely form a huge series of alloy systems larger than that shown in Fig. 6. In all the structures, Mg, which has a small atomic radius, partially occupies the rare earth sites of the AB$_2$ unit; these sites are difficult for rare earth metals with larger atomic radii to wholly occupy. The consequence is that a stable structure is formed.

For the above reasons, the system is considered to be a stable hydrogen storage alloy in which phenomena such as disproportionation due to the repetition of hydrogenation and dehydrogenation do not progress. Research on the improvement of hydrogen storage properties by replacing elements in the Laves layer with elements other than Mg will be necessary in the future.

4. Conclusions

We investigated the crystal structures of hydrogen storage alloys with a new La–Mg–Ni–Co system and discovered the existence of three kinds of structure.

Alloy T1 (composition: La$_{0.76}$Mg$_{0.24}$Ni$_{12.95}$Co$_{0.05}$) was composed of main phases with structures similar to those of Ce$_2$Ni$_7$ and PuNi$_3$ types. Alloy T2 (composition: La$_{0.76}$Mg$_{0.24}$Ni$_{13.07}$Co$_{0.50}$) was composed of main phases with structures similar to those of Ce$_2$Ni$_7$ and Pr$_5$Co$_{10}$ types. The Ce$_2$Ni$_7$ type (composition: La$_{0.8}$Mg$_{0.2}$Ni$_{12.95}$Co$_{0.05}$) was hexagonal with lattice constants $a = 0.5052(1)$ nm, $c = 2.4245(3)$ nm. The PuNi$_3$ type (composition: La$_{0.7}$Mg$_{0.2}$Ni$_{12.95}$Co$_{0.05}$) had lattice constants $a = 0.5062(1)$ nm, $c = 2.4500(2)$ nm with a hexagonal axis. The stable structure of the La$_2$Mg$_3$(Ni, Co)$_{10}$ was not the 3R-type Ce$_2$Ni$_7$-type structure reported for La$_2$Ni$_{10}$, but a 2H-type structure. This composition, La$_{0.8}$Mg$_{0.2}$Ni$_{12.95}$Co$_{0.05}$, was hexagonal, with lattice constants $a = 0.5042(2)$ nm, and $c = 3.2232(3)$ nm.
Structural study of the La–Mg–Ni–Co system alloys revealed a material group with versatile layered structures. All of these phases were composed of a single Laves layer and several [CaCu₅] layers stacked along the c-axis. A wide variety of layered structures can be established, depending on the combinations of stacked layers. Mg atoms enter the La sites of the Laves layer and eliminate the strain generated in stacking with the [CaCu₅] layer, thus helping to stabilize the structure.

Consequently, this system may have excellent hydrogen storage properties that it may not be susceptible to the progressive disproportionation caused by repeated absorption and desorption of hydrogen. If it is feasible to synthesize a design capable of controlling layer stacking at will, then this new material group may be useful as hydrogen storage alloys in which high performance can be achieved through control of the layer structure.

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