In–situ powder neutron diffraction study on the formation process of LaMg$_2$NiH$_7$

Toyoto Sato$^a$, Kazutaka Ikeda$^b$, Motoaki Matsu$^c$, Kazutoshi Miwa$^d$, Toshiya Otomo$^{b,e}$, Stefano Deledda$^f$, Bjørn C. Hauback$^f$, Guanqiao Li$^g$, Shigeyuki Takagi$^a$, Shin–ichi Orimo$^{a,g}$

Affiliations

$^a$Institute for Materials Research, Tohoku University, Japan
$^b$Institute of Materials Structure Science, High Energy Accelerator Research Organization, Japan
$^c$School of Science and Technology, Kwansei Gakuin University, Japan
$^d$Toyota Central Research & Development Laboratories, Inc., Japan
$^e$Department of Materials Structure Science, The Graduate University for Advanced Studies, Japan
$^f$Physics Department, Institute for Energy Technology, Norway
$^g$WPI–Advanced Institute for Materials Research, Tohoku University, Japan.

*Corresponding author. Tel.: +81–(0)22–215–2094; fax: +81–(0)22–215–2091. E–mail: toyoto@imr.tohoku.ac.jp

Abstract

The formation process from the intermetallic compound LaMg$_2$Ni to a complex hydride (deuteride) LaMg$_2$NiD$_x$ composed of La$^{3+}$, 2×Mg$^{2+}$, [NiD$_4$]$^{4–}$, and 3×D$^–$ was investigated by in–situ powder neutron diffraction under deuterium gas pressure at room temperature. Below 0.001 MPa, small amount of deuterium was initially dissolved in the lattice of LaMg$_2$Ni forming LaMg$_2$NiD$_{0.05}$ and two new hydride phases (LaMg$_2$NiD$_{1.4}$ and LaMg$_2$NiD$_{1.9}$) were continuously yielded. Furthermore, LaMg$_2$NiD$_{4.6}$ with NiD$_{1.9}$ and NiD$_{3.3}$ units and interstitial deuterium atoms was formed prior to appearing of LaMg$_2$NiD$_7$. From their Bragg peak positions, the deuterium contents $x_1$, and $x_2$ were inferred as 0.05 < $x_1$ < $x_2$ < 4.6. At approximately 0.001 MPa, LaMg$_2$NiD$_7$ started forming. Since the intermediate deuterides had similar metal atomic framework of LaMg$_2$Ni, we revealed that LaMg$_2$NiD$_7$ formation proceeded through multiple deuteride phases with maintaining of the metal atomic framework of LaMg$_2$Ni.

Keywords: In–situ powder neutron diffraction; Complex hydride; Crystal structure
Introduction

Complex hydrides are composed of metal cation(s) such as Li⁺ and Mg²⁺ and complex anion(s) such as [BH₄]⁻ and [NiH₄]⁺, in which the hydrogen atoms act as ligand covalently bond to the central atom. The complex hydrides are attractive due to a wide variety of functionalities, such as hydrogen storage, superconductivity, fast ionic conductivity, magnetism, and metal–insulator transition [1–6].

Although the formation process of complex hydrides is of both fundamental and technological interest in order to further understand such functionalities, it remains incompletely understood because of the large accompanying reconstructions of the metal atomic frameworks. For instance, a complex hydride YMn₂H₆, in which Y is coordinated by four Mn ((MnH₆)₅⁻), is yielded from YMn₂, in which Y is coordinated by twelve Mn (Laves polyhedron) [7]. In contrast, the complex hydride LaMg₂NiH₇ reported by Yvon et al., composing of La₃⁺, 2×Mg²⁺, [NiH₄]⁺, and 3×H⁻, is formed from an intermetallic compound LaMg₃Ni where the metal atomic framework of LaMg₂Ni is maintained (Fig. 1) [8–11]. Then, the formation process of LaMg₂NiH₇ is suggested to infer from the atomic arrangements in the same manner that many interstitial hydrides have been investigated. From our recent investigations on the hydrogenation reaction of LaMg₂Ni, we discovered that LaMg₂NiH₇ formation was preceded by an intermediate phase LaMg₂NiH₄.₆ [12]. Using powder neutron diffraction (PND) on a deuteride analog prepared in an ex–situ experiment, LaMg₂NiH₄.₆ was elucidated to adopt a monoclinic crystal structure (a = 8.592 Å, b = 7.995 Å, c = 6.099 Å, and β = 99.318° in the space group P2₁/m (No. 11)) with NiH₁.₉ and NiH₃.₃ units, and interstitial hydrogen atoms (see Fig. 1). The NiH₁.₉ and NiH₃.₃ units have similar atomic arrangements as the complex anion [NiH₄]⁺ in LaMg₂NiH₄. Theoretical calculations, LaMg₂NiH₄.₆ was confirmed to be a metallic hydride and the results showed to be the covalent bonding between Ni and H in the NiH₁.₉ and NiH₃.₃ units. Thus, the NiH₁.₉ and NiH₃.₃ units could be the basis for the formation of the complex anion [NiH₄]⁺ in LaMg₂NiH₇. Such units have also been reported in hydrides of rare earth and transition metals (e.g., Ce₂NiH₄.₇), MgNi₂H₃ and Pd–based complex hydrides (e.g., Li₂PdH₉) [13–19]. Since the NiH₁.₉ and NiH₃.₃ units were reminiscent of [NiH₄]⁺ and similar to their related hydrides, they were suggested to be precursors for formation of the complex anion [NiH₄]⁺ in our previous work [12].

In this study, we performed an in–situ PND experiment under deuterium gas pressure to directly observe and further elucidate details of the formation process from LaMg₂Ni to LaMg₂NiD₇.
Experimental methods

LaMg$_2$Ni was prepared by induction melting of a mixture of La ingots (Sigma–Aldrich, 99.9%) and Mg$_2$Ni powder (Kojundo Chemical Laboratory, 99.9%) in a molar ratio of 1:1. The details are described in ref. 12.

The in–situ PND experiment was performed at room temperature under deuterium gas pressure (<5 MPa) on the NOVA at the Material and Life Science Experimental Facility (MLF) of the Japan Proton Accelerator Research Complex (J–PARC), Japan. LaMg$_2$Ni (1.8142 g) was filled in a cylindrical single–crystal sapphire sample container with an outside diameter and thickness of 10.8 mm and 2.5 mm, respectively. The deuterium gas was loaded to the cylindrical single–crystal sapphire sample container every 4 h and the deuterium gas pressure was gradually increased up to 5 MPa. In this paper, deuterium gas pressure refers to 4 h later after the deuterium loading. PND patterns were obtained from the detectors of medium resolution ($\Delta d/d \approx 0.6\%$) with the scattering angles $2\theta = 72–108^\circ$ every 4 h. Subtraction of the contribution of the sample container was performed with separately measured diffraction data of container without sample. The detector pixels contain Bragg peaks of the single–crystal sapphire were identified and these pixels were not used in the data analysis. The PND patterns included the contribution from the sample container, which was separately observed by NOVA at room temperature, then subtracted.

The unit cell parameters were calculated by the indexing programs TREOR97 [20] and PIRUM [21] and the Rietveld analysis was performed using the GSAS software with the graphical interface EXPGUI (version 1.80) [22] on the PND data with d–spacing = 0.66 to 6.55 Å. Profile function developed by Von Dreele et al was used for the Rietveld analysis [23]. The background was modeled by 16–terms Chebyshev polynomial function model in GSAS.

The sample was handled in Ar or He gas filled glove boxes with a dew point below 183 K and with less than 1 ppm of O$_2$ to prevent (hydro–) oxidation.

Results and discussion

Figure 2 shows PND patterns under deuterium gas pressures from below 0.001 to 4.34 MPa at room temperature. The minimum measurable pressure is 0.001 MPa in this experiment. In this paper, we refer pressures lower than the minimum measurable pressure to below 0.001 MPa. The data are compared with the simulated PND patterns of LaMg$_2$Ni, LaMg$_2$NiD$_{4.6}$, and LaMg$_2$NiD$_7$, respectively. It is observed shifts in Bragg peak positions, new Bragg peaks appear, and Bragg peaks of LaMg$_2$NiD$_{4.6}$ and LaMg$_2$NiD$_7$ are observed already at deuterium pressure below 0.001 MPa and at room
temperature. These peak shifts and presence of new peaks were not observed in our previous ex situ experiment [12]. This suggests that LaMg2Ni starts absorbing deuterium below 0.001 MPa and with changes in the crystal structure. The deuteration reaction temperature and pressure are much lower than in previous reports [8–12]. The remaining LaMg2NiD4.6, which is approximately 30 wt.% in the PND analyzed by the Rietveld refinement, at 4.34 MPa is attributed to the slow kinetics of the deuteration reaction from LaMg2NiD4.6 to LaMg2NiD7 at room temperature. This reaction was completed at higher temperatures in the hydride analog LaMg2NiH4.6.

The formation process from LaMg2Ni to LaMg2NiD7 proceeds by three steps: (1) an initial deuteration reaction starting immediately in 4 h after deuterium gas loading, (2) an intermediate reaction below 0.001 MPa (32 h later after deuterium gas loading), and (3) final formation above 0.001 MPa. In the (1) and (2) steps, pressures are below minimum measurable range (0.001 MPa). We first address the unit cell parameters of LaMg2Ni during (1) the initial deuteration reaction. The unit cell parameters of LaMg2Ni as a function of time after deuterium gas loading are plotted in Fig. 3 and they are listed in Table 1. Prior to deuterium gas loading, the Bragg peaks on the PND pattern are indexed by an orthorhombic unit cell with $a = 4.2120(5) \text{ Å}$, $b = 10.2626(14) \text{ Å}$, and $c = 8.3428(12) \text{ Å}$, which corresponds to LaMg2Ni [8, 9]. Following the deuterium gas loading, the $a$– and $c$–axes are slightly elongated and shortened respectively, while the $b$–axis is almost unchanged by dissolution of deuterium in the lattice of LaMg2Ni. In order to clarify if deuterium atoms are dissolved in the lattice of LaMg2Ni, Rietveld analysis on the PND pattern 4 h after deuterium gas loading was performed. The stoichiometry of the deuterium dissolved phase is determined as LaMg2NiD0.05 with deuterium located on a tetrahedral site coordinated by two La and two Mg atoms, and on a site coordinated by one La and two Mg atoms (the crystallographic parameters and Rietveld refinement fits are shown in Supplementary material). Such deuterium dissolved phases have also been reported in the initial deuteration reactions of the intermetallic compounds LaNi5 and Mg2Ni, which form LaNi5D0.3 [24] and Mg2NiD0.3 [25], respectively. The volume expansions is much smaller in LaMg2NiD0.05 (less than 0.1%) than in LaNi5D0.3 (0.4%) and Mg2NiD0.3 (4%). Even for the fully deuterided phases, the volume expansions in LaMg2NiD7 (19%) is significantly smaller than in LaNi5D6 (25%) and Mg2NiD4 (32%). In the initial intermetallics the distances between the metal atoms in LaMg2Ni is bigger than in LaNi5 and Mg2Ni. The shortest interatomic distances are listed in Table 2. This suggests that LaMg2Ni has more voids for accommodation of deuterium (hydrogen) atoms in the crystal structure than LaNi5 and Mg2Ni. Therefore, the lower volume expansion on deuteration (hydrogenation) reaction
of LaMg₂Ni could originate from additional spaces in the crystal structures of the initial intermetallic compounds.

The next part is the deuteration reaction under deuterium gas pressure below 0.001 MPa after 4 h. In this deuterium gas pressure range, two new phases and LaMg₂NiD₄.6 are identified. Prior to LaMg₂NiD₄.6 formation, two unknown Bragg peaks appear at approximately \( d = 3.65 \text{ Å} \) and \( d = 3.70 \text{ Å} \) (marked by yellow and purple arrows, respectively, in Fig. 2). The Bragg peak at \( d = 3.65 \text{ Å} \) appears before the peak at \( d = 3.70 \text{ Å} \), indicating that the two peaks originate from different phases. Here, we refer to the phases with peaks at \( d = 3.65 \text{ Å} \) and \( d = 3.70 \text{ Å} \) as LaMg₂NiD₁₁ and LaMg₂NiD₂₂, respectively. The Bragg peaks with weak intensities related to LaMg₂NiD₁₁ and LaMg₂NiD₂₂ are limited in number, and thus their crystal structures are difficult to elucidate. All observed Bragg peak positions of LaMg₂NiD₁₁ and LaMg₂NiD₂₂ in \( d \)-spacing = 0.66–8.05 Å are close and appear at lower \( d \)-spacing than for LaMg₂NiD₄.6. This suggests that LaMg₂NiD₁₁, LaMg₂NiD₂₂ and LaMg₂NiD₄.6 have similar crystal structures. Assuming the similarity of the crystal structures, the hydrogen contents of LaMg₂NiD₁₁ and LaMg₂NiD₂₂ are suggested to be 0.05 < \( x_1 < x_2 < 4.6 \). At this stage of the reaction, the deuterium atoms in LaMg₂NiD₁₁ and LaMg₂NiD₂₂ could be located in interstitial sites close to the Ni atoms as LaMg₂NiD₄.6 (Fig. 1).

Above approximately 0.001 MPa, both LaMg₂NiD₁₁ and LaMg₂NiD₂₂ disappear and the deuteration reaction proceeds from LaMg₂NiD₄.6 to LaMg₂NiD₇. During the reaction, neither Bragg peak shifts nor unknown Bragg peaks are observed, indicating the direct formation of LaMg₂NiD₇ from LaMg₂NiD₄.6 under this condition. As mentioned above, LaMg₂NiD₄.6 and LaMg₂NiD₇ adopt similar metal atomic frameworks to LaMg₂Ni (see Fig. 1). Thus, we have revealed that LaMg₂NiD₇ forms through multiple deuteride phases with similar metal frameworks of LaMg₂Ni.

Conclusions
We have performed an in–situ PND experiment at deuterium gas pressures below 5 MPa at room temperature. The experiment directly and precisely revealed the formation process from LaMg₂Ni to LaMg₂NiD₇ composed of La³⁺, 2×Mg²⁺, [NiD₄]⁺, and 3×D⁻. Even at room temperature, LaMg₂Ni started absorbing deuterium below 0.001 MPa, forming a deuterium dissolved phase (LaMg₂NiD₀.00). Continuously, two new phases were identified (LaMg₂NiD₁₁ and LaMg₂NiD₂₂). After the formation of those deuteride phases, LaMg₂NiD₄.6 with NiD₁₉ and NiD₃₃ units, and interstitial deuterium atoms was formed. The Bragg peak positions of LaMg₂NiD₁₁ and LaMg₂NiD₂₂ implied that their crystal structures including deuterium atomic positions resembled that of
LaMg$_2$NiD$_{4.6}$, but with lower deuterium contents than LaMg$_2$NiD$_{4.6}$ (0.05 < $x_1 < x_2 < 4.6$). In the final reaction step, LaMg$_2$NiD$_{4.6}$ was formed into LaMg$_2$NiD$_7$. Thus, the in–situ PND experiment revealed that LaMg$_2$NiD$_7$ forms via multiple deuteride phases, in which the deuterium atoms were first dissolved in the lattice of LaMg$_2$Ni, then locate in the interstitial sites and around the Ni atoms, and finally become covalently bonded to Ni, forming the complex anion [NiD$_4$]$^{4-}$.

Highlight
- Formation process of a complex hydride (deuteride) LaMg$_2$NiD$_7$
- Crystal structure changes during the hydrogenation (deuteration) reaction
- In–situ powder neutron diffraction experiments under deuterium gas pressure

Acknowledgements
We are grateful for technical support from H. Ohmiya and N. Warifune. This work was supported by JSPS KAKENHI (Grant No. 16K06766, 16H06119 and 25220911) and Collaborative Research Center on Energy Materials in IMR (E–IMR). The neutron scattering experiment was approved by the Neutron Science Proposal Review Committee of J–PARC/MLF (Proposal No. 2014A0200).
References


Table 1 Unit cell parameters of LaMg$_2$Ni at the initial deuteration reaction. Estimation of unit cell parameters (32 h) are not allowed due to less number of the Bragg peaks.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.2120(5)</td>
<td>10.2626(14)</td>
<td>8.3428(11)</td>
</tr>
<tr>
<td>4</td>
<td>4.2171(3)</td>
<td>10.2649(14)</td>
<td>8.3353(12)</td>
</tr>
<tr>
<td>8</td>
<td>4.2172(8)</td>
<td>10.2656(15)</td>
<td>8.3353(14)</td>
</tr>
<tr>
<td>12</td>
<td>4.2169(8)</td>
<td>10.2648(16)</td>
<td>8.3354(13)</td>
</tr>
<tr>
<td>16</td>
<td>4.2166(8)</td>
<td>10.2663(14)</td>
<td>8.3357(13)</td>
</tr>
<tr>
<td>20</td>
<td>4.2177(11)</td>
<td>10.2652(19)</td>
<td>8.3343(12)</td>
</tr>
<tr>
<td>24</td>
<td>4.2178(16)</td>
<td>10.2641(20)</td>
<td>8.3348(15)</td>
</tr>
<tr>
<td>28</td>
<td>4.2173(24)</td>
<td>10.2609(28)</td>
<td>8.3336(30)</td>
</tr>
</tbody>
</table>

Table 2 The shortest interatomic distances of each constituent element on LaMg$_2$Ni, LaNi$_5$ and Mg$_2$Ni

<table>
<thead>
<tr>
<th></th>
<th>LaMg$_2$Ni</th>
<th>LaNi$_5$</th>
<th>Mg$_2$Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>2.95 Å (La–Ni)</td>
<td>2.90 Å (La–Ni)</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>2.77 Å (Mg–Ni)</td>
<td></td>
<td>2.65 Å (Mg–Ni)</td>
</tr>
<tr>
<td>Ni</td>
<td>2.77 Å (Ni–Mg)</td>
<td>2.46 Å (Ni–Ni)</td>
<td>2.60 Å (Ni–Ni)</td>
</tr>
</tbody>
</table>
Figure captions

Figure 1 (Left) Crystal structures and (right) local atomic arrangements around Ni atom of (top) LaMg$_2$Ni, (middle) LaMg$_2$NiH$_{4.6}$ and (bottom) LaMg$_2$NiH$_7$ [8, 9, 12]. Gray, orange, green, blue circles indicate La, Mg, Ni and H, respectively.

Figure 2 Powder neutron diffraction patterns under deuterium gas pressure of < 5 MPa at room temperature. Black, green, red and blue lines indicate experimentally observed and simulated powder neutron patterns of LaMg$_2$Ni, LaMg$_2$NiD$_{4.6}$ and LaMg$_2$NiD$_7$, respectively. Bragg peaks of LaMg$_2$NiD$_{x1}$ and LaMg$_2$NiD$_{x2}$ are marked by yellow and purple arrows, respectively.

Figure 3 Unit cell parameters of LaMg$_2$Ni as a function of time at the initial deuteration reaction. Estimation of unit cell parameters (32 h) are not allowed due to less number of the Bragg peaks.
Figure 1 (Left) Crystal structures and (right) local atomic arrangements around Ni atom of (top) LaMg$_2$Ni, (middle) LaMg$_2$NiH$_{4.6}$ and (bottom) LaMg$_2$NiH$_7$ [8, 9, 12]. Gray, orange, green, blue circles indicate La, Mg, Ni and H, respectively.
Figure 2 Powder neutron diffraction patterns under deuterium gas pressure of < 5 MPa at room temperature. Black, green, red and blue lines indicate experimentally observed and simulated powder neutron patterns of LaMg$_2$Ni, LaMg$_2$NiD$_{4.6}$ and LaMg$_2$NiD$_{7}$, respectively. Bragg peaks of LaMg$_2$NiD$_{4.1}$ and LaMg$_2$NiD$_{5.2}$ are marked by yellow and purple arrows, respectively.
Figure 3

Figure 3 Unit cell parameters of LaMg₂Ni as a function of time at the initial deuteration reaction. Estimation of unit cell parameters (32 h) are not allowed due to less number of the Bragg peaks.