MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2017A0115 実験課題名 Title of experiment Observation of hydrogen release reaction on a complex hydride 実験責任者名 Name of principal investigator Toyoto sato 所属 Affiliation Tohoku university	装置責任者 Name of responsible person Toyoto Sato 装置名 Name of Instrument/（BL No.） NOVA (BL-21) 実施日 Date of Experiment 2017 June 4 – 7

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Lanthanum magnesium nickel deuteride, $LaMg_2NiD_7$, Powder

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Complex hydrides, which is composed of metal cation(s) such as Mg^{2+} and complex anion(s) such as $[NiH_4]^{4-}$ with covalent bonding between the central atom and the hydrogen, have attracted due to a wide variety of functionalities, such as hydrogen storage materials and so on [S. Orimo, et al., Chem. Rev. 107, 4111, (2007).].

Although formation (hydrogenation) and decomposition (hydrogen release) reaction processes of the complex hydrides are of both fundamental and technological interest in order to further understand such functionalities, the reaction processes is difficulty in understanding because most of complex hydrides generally show large rearrangements of metal atomic frameworks during the reactions. In contrast, a complex hydride $LaMg_2NiH_7$ composed of La^{3+}, $2\times Mg^{2+}$, $[NiH_4]^{4-}$ and $3\times H^-$ is formed from a ternary intermetallic compound $LaMg_2Ni$ with maintaining of the metal atomic frameworks under hydrogen gas pressure (Fig. 1). Focusing on the hydrogenation reaction process from $LaMg_2Ni$ to $LaMg_2NiH_7$ with maintaining of metal atomic frameworks, we recently discovered an intermediate phase $LaMg_2NiH_{4.6}$ with NiH_x units (x = 2 and 3) (Fig. 1), which was yielded before formation of $LaMg_2NiH_7$, by using neutron diffraction experiments combined with theoretical calculations [K. Miwa, T. Sato et al., J. Phys. Chem. C 120, 5926, (2016).].

2. 実験方法及び結果（つづき） Experimental method and results (continued)

The NiH_x units showed similar Ni and H atomic arrangements and covalent bonding of Ni–H to a complex anion $[NiH_4]^{4-}$ in $LaMg_2NiH_7$. Thus, those units could be suggested as precursor units for formation of $[NiH_4]^{4-}$. In addition, we could successfully observe hydrogenation (deuteration) reaction process of $LaMg_2Ni$ viewed from the crystal structure by in–situ neutron powder diffraction under deuterium gas pressure (≤ 5 MPa) using NOVA (2014A0200) [T. Sato et al., Int. J. Hydrogen Energy in press]. Though those results revealed the hydrogenation reaction process of $LaMg_2Ni$ ($LaMg_2NiH_7$), the hydrogen release reaction has been yet to be completely understood.

In this study, we therefore performed powder neutron diffraction experiments on $LaMg_2NiD_7$ upon heating (10–450 K) under vacuum using NOVA (BL–21) for understanding of deuterium release reaction of $LaMg_2NiD_7$. Powder of $LaMg_2NiD_7$ (1.1644 g) was synthesized from $LaMg_2Ni$ in D_2 pressure of 1 MPa at 473 K for 12h and filled in a cylindrical null-scattering $V_{96}Ni_4$ alloy sample container with an outside diameter and thickness of 6.0 mm and 0.1 mm, respectively. Rietveld refinement on powder neutron diffraction patterns was performed using the GSAS software with the graphical interface EXPGUI (version 1.80).

Figure 2 shows Rietveld refinement fits on the powder neutron diffraction observed at 10 K. The experimentally observed powder neutron diffraction pattern was reasonably reproduced by a crystal structure of $LaMg_2NiD_7$ with a monoclinic structure with a = 13.9839(7) Å, b = 4.6905(2) Å, c = 16.0312(7) Å and β = 125.242(2)° in the space group $P2_1/c$ (No. 14). Furthermore, all powder neutron diffraction patterns up to 450 K were also analyzed by Rietveld refinements. From the Rietveld refinement results, crystallographic parameters on $LaMg_2NiD_7$ before deuterium releasing change with increasing temperature. Those results would relate to deuterium release reaction of $LaMg_2NiD_7$.

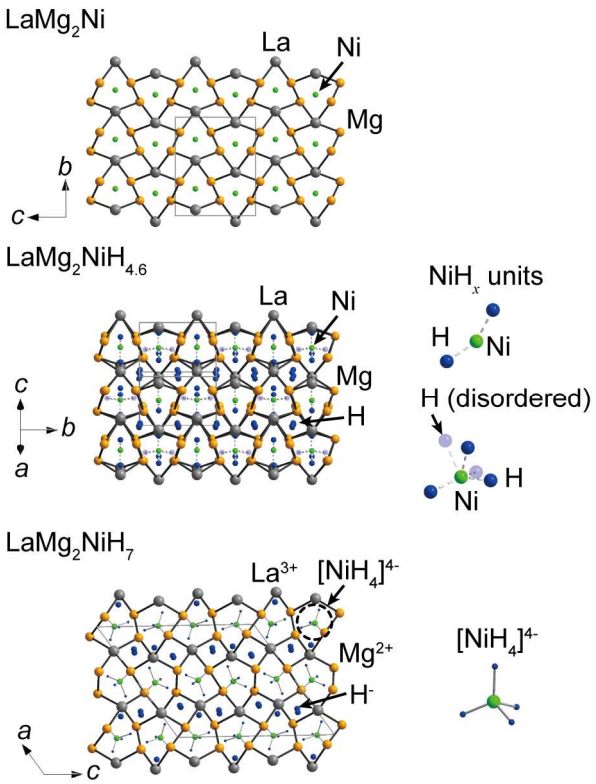

Fig. 1 Crystal structures and local atomic arrangements around Ni of (top) $LaMg_2Ni$, (middle) $LaMg_2NiH_{4.6}$ and (bottom) $LaMg_2NiH_7$. Gray, orange, green and blue circles indicate La, Mg, Ni and H, respectively.

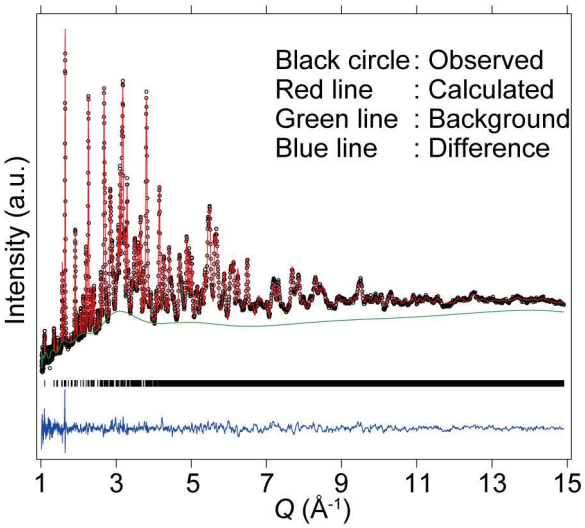

Fig. 2 The Rietveld refinement fit of the powder neutron diffraction for $LaMg_2NiD_7$ observed at 10 K (R_{wp} = 0.0067). The observed, calculated, background and difference between observed and calculated are indicated black circles, a red, green and blue lines, respectively.