| MLF Experimental Report | 提出日 Date of Report |
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| 課題番号 Project No.<br>2014A0200<br>実験課題名 Title of experiment<br>Formation and Decomposition Processes of Metal–Deuterium Bonds between $LaMg_2Ni$ and $LaMg_2NiD_7$ Studied by in–situ Powder Neutron Diffraction<br>実験責任者名 Name of principal investigator<br>Toyoto Sato<br>所属 Affiliation<br>Tohoku University | 装置責任者 Name of responsible person<br>Otomo Toshiya<br>装置名 Name of Instrument/(BL No.)<br>NOVA (BL21)<br>実施日 Date of Experiment<br>2014 May 29– June 02 |

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, $LaMg_2Ni$, 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.

$LaMg_2Ni$ has been reported to form $LaMg_2NiH_7$ in a hydrogen gas pressure of 0.8 MPa at 473 K [Phys. Rev. Lett. 94 (2005) 066403.]. Figure 1 shows crystal structures of $LaMg_2Ni$ and $LaMg_2NiH_7$. Although both compounds have different crystal systems ($LaMg_2Ni$: orthorhombic ($a$ = 4.227 Å, $b$ = 10.303 Å, $c$ = 8.360 Å; $LaMg_2NiH_7$: monoclinic ($a$ = 13.979 Å, $b$ = 4.703 Å, $c$ = 16.025 Å, $\beta$ = 125.240°)), they adopt similar frameworks of metal atomic arrangements. In the frameworks, $LaMg_2NiH_7$ show slightly distorted from $LaMg_2Ni$ as typical interstitial–type hydrides in which hydrogen atoms are located at interstitial sites surrounded by metal atoms.

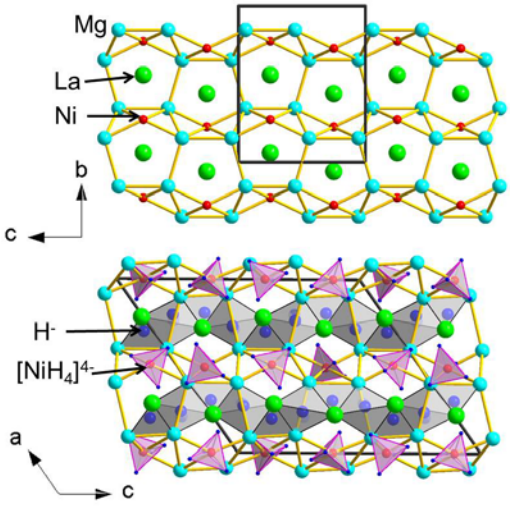


Figure 1 Crystal structures of (top) $LaMg_2Ni$ and (bottom) $LaMg_2NiH_7$

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

On the contrary, $LaMg_2NiH_7$ is not classified into the interstitial-type hydrides because it interestingly has two different kinds of hydrogen – metal interactions which are tetrahedral $[NiH_4]^{4-}$ complex anion (H atoms are covalently bonded with Ni atom) and $H^-$ (H atom is surrounded by Mg and La atoms). Even though many types of hydrides have been reported, coexistence of such two different kinds of the bonding state associated with hydrogen is in rare cases.

For the reason, this is one good hydride for understanding of the bonding state associated with hydrogen. Though researchers have clarified the hydrogen absorption and desorption properties and crystal and electronic structures and materials properties on $LaMg_2NiH_7$ [K. Yvon et al., Phys. Rev. Lett. 94 (2005) 066403.; M.D. Chio, et al., intermetallics 16 (2008) 102.; A. Teresiak et al., J. Alloys Compd. 481 (2009) 144.], the formation process of the hydride from the viewpoint of the interaction between metal and hydrogen has not been reported in spite of indispensable for development of hydrogen storage materials.

Therefore, we have carried out the in-situ neutron diffraction experiments on $LaMg_2Ni$ in deuterium atmosphere at NOVA (BL-21) in order to elucidate the formation processes of the two different bonding states associated with deuterium in $LaMg_2NiD_7$.

Approximately 2.0 g of $LaMg_2Ni$, which was synthesized by an induction furnace, was placed in a quartz container with an inside diameter of 6 mm for the neutron diffraction experiments. In our preliminary experiment at our laboratory, $LaMg_2Ni$ quickly formed $LaMg_2NiH_7$ at 473 K in the hydrogen gas pressure of 1 MPa. The quick hydrogenation reaction was guessed to prevent from elucidation of the hydrogenation reaction. However, $LaMg_2Ni$ gradually showed hydrogenation reaction and formed $LaMg_2NiH_7$ at room temperature in a hydrogen atmosphere. Therefore, the neutron diffraction experiments were carried out at 303 K in a deuterium gas pressure of ≤ 5 MPa.

Figure 2 shows the neutron diffraction patterns before and after deuteration reaction of $LaMg_2Ni$ with a simulated neutron diffraction pattern of $LaMg_2NiD_7$. The neutron diffraction pattern indicates that $LaMg_2Ni$ surely formed $LaMg_2NiD_7$ at room temperature in a deuterium atmosphere. This is that $[NiH_4]^{4-}$ complex anion was formed at room temperature. In addition, minor unknown peaks are also identified. Presently, the neutron diffraction patterns are analyzed by Rietveld method [R. Oishi et al., Nucl. Instrum. Methods A 600 (2009) 94.] in order to elucidate the unknown phase and the formation processes of $LaMg_2NiD_7$ from $LaMg_2Ni$.

The dehydrogenation (hydrogen release reaction) of $LaMg_2NiD_7$ showed at around 523 K in vacuum and $LaD_x$ and $Mg_2Ni$ were yielded.

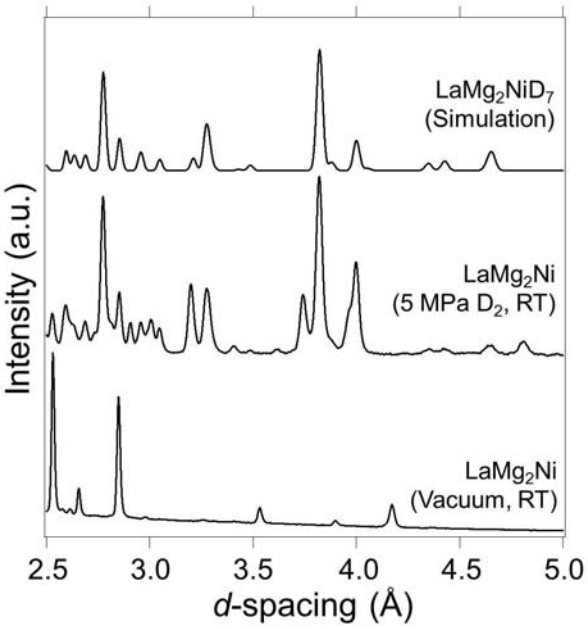


Figure 2 Neutron diffraction patterns of $LaMg_2Ni$ In vacuum (0.0001 MPa) and a deuterium gas pressure of 5 MPa and simulated neutron diffraction pattern of $LaMg_2NiD_7$