Observation of Hydrogen Absorption/Desorption Reaction Processes in Li-Mg-N-H System by in-situ X-ray Diffractmetry

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ABSTRACT

The in-situ XRD measurements on dehydrogenation/rehydrogenation of the Li-Mg-N-H system were performed in this work. The ballmilled mixture of 8LiH and $3Mg(NH_2)_2$ as a hydrogenated phase gradually changed into Li_2NH as a dehydrogenated phase during heat-treatment at 200 °C in vacuum for 50 h. Neither Mg-related phases nor other intermediate phases were recognized in the dehydrogenated phase. With respect to the hydrogenation process, the dehydrogenated state gradually returned to the mixed phase of the LiH and $Mg(NH_2)_2$ without appearance of any intermediate phases during heat treatment at 200 °C under 5 MPa H_2 for 37 h and during slow cooling down to room temperature through 24 h. In the hydrogenation process at 200 °C under 1 MPa H_2, however, the growing up of the $LiNH_2$ and LiH phase was observed in the XRD profiles before the $3Mg(NH_2)_2$ and 8LiH phases were formed as the final hydrogenated state. This indicates that the $LiNH_2$ and LiH phase essentially appears as an intermediate state in the Li-Mg-N-H system composed of $3Mg(NH_2)_2$ and 8LiH.

Keywords: hydrogen absorbing materials, crystal growth, gas-solid reactions, X-ray diffraction

Introduction

The research of metal-N-H system as one of the hydrogen storage (H-storage) materials was first performed in 2002 by Chen *et al.* with examining the H-storage properties of Li_3N [1]. Since then, many related studies have been reported all over the world [2~14]. Ichikawa *et al.* have employed the following reaction as H-storage, which corresponds to a part of the H-storage reaction of Li_3N [2],

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2 \qquad (1).$$

They claimed that the above dehydrogenation reaction is not a direct molecule-molecule reaction between $LiNH_2$ and LiH, but it can be expressed by an ammonia mediating model [7,15]. By analogy with this model, Leng *et al.* have designed and developed a new Li-Mg-N-H system based on the ammonia mediating model, in which $Mg(NH_2)_2$ instead of $LiNH_2$ is used as an ammonia provider [16]. Since $Mg(NH_2)_2$ is thermodynamically less stable than $LiNH_2$, ammonia is emitted more easily than $LiNH_2$, and gaseous hydrogen is desorbed at lower temperature by the interaction between LiH and NH_3 provided by the decomposition of $Mg(NH_2)_2$. The Li-Mg-N-H system designed by Leng *et al.* is composed of $3Mg(NH_2)_2$ and 8LiH, and desorbs hydrogen up to ~7 mass% H_2 at 140 ~ 200 °C under a helium gas flow. Incidentally, the H-storage properties of Li-Mg-N-H systems with other mixing ratios of $Mg(NH_2)_2$ and LiH have been independently reported by Luo [17] and Xiong, *et al.* ($Mg(NH_2)_2$: LiH = 3:6) [18] and Nakamori, *et al.* ($Mg(NH_2)_2$: LiH = 3:12) [19] at almost the same period.

Here, the chemical reaction of the Li-Mg-N-H system designed by Leng *et al.* is expressed as follows;

$$3Mg(NH_2)_2 + 8LiH \leftrightarrow Mg_3N_2 + 4Li_2NH + 8H_2 \qquad (2).$$

The reversibility of this reaction has been confirmed by repeating dehydrogenation and rehydrogenation at 200 °C in vacuum and 3MPa H_2, respectively. The hydrogenation properties of the Li-Mg-N-H system ($Mg(NH_2)_2$: LiH = 3:8) investigated by Ichikawa *et al.*[20] revealed that the product could not be fully hydrogenated at 150 °C under 10 MPa H_2, while the pressure-composition isotherm (PCI) at 200 °C reveals two-step hydrogenation process under equilibrium conditions at 200 °C. A mechanism of hydrogenating reaction on the basis of ammonia mediating model has been proposed by Leng, *et al.* [21], which is given by the following reactions:

$$Li_2NH + H_2 \rightarrow LiNH_2 + LiH \qquad (3)$$

$$2LiNH_2 \rightarrow Li_2NH + NH_3 \qquad (4)$$

$$Mg_3N_2 + 4NH_3 \rightarrow 3Mg(NH_2)_2 \qquad (5).$$

As another mechanism model, Xiong, *et al.* have proposed a direct molecule-molecule reaction model, in which the dehydrogenation reaction proceeds by a direct reaction between the LiH and the $Mg(NH_2)_2$ molecules [18].

As a basis of understanding a disproportionation reaction, it is one of the most interesting issues to know which reaction mechanism is realized in this system. If the reaction process is directly observed, the reaction model may be clarified. On the motivation of those features, we tried to perform the in-situ X-ray diffraction measurement under a suitable condition with controlling temperature and atmosphere in the Li-Mg-N-H system. In our group, special attention has been paid to the system with $3Mg(NH_2)_2$ and 8LiH to clarify time evolution of the starting and final phases in the reaction (2) and appearance of some intermediate phases, and to research the origin of the two-step process in PCI at 200 °C.

Experimental

The starting materials, LiH (95 mass% purity) and MgH_2 (90 mass% purity, 9 mass% is unreacted Mg and the rest of 1 mass% is other impurities) were purchased from Sigma Aldrich. In this work, $Mg(NH_2)_2$ was synthesized by mechnaically milling MgH_2 in pure NH_3 gas of 0.4 MPa. The mechanical milling for preparing $Mg(NH_2)_2$ was performed for 12 h at room temperature using a rocking mill equipment (SEIWA GIKEN Co., Ltd. RM-10) with a frequency of 10 Hz. Prior to the in-situ XRD measurement, 300 mg of the mixture of $3Mg(NH_2)_2$ and 8LiH with 1 mol% of $TiCl_3$[22], was milled with 20 steel balls (diameter: 7 mm) for 4 h at room temperature under a hydrogen atmosphere of 1 MPa, using a planetary ball mill equipment (Fritsch, P7) at 400 rpm. The XRD equipment was a RINT-2000 type designed by Rigaku with a sample holder which can control temperature and pressure up to 300 (500) °C and 5 (3) MPa, respectively. The measurement condition was 40 kV and 200 mA with CuKα radiation. In the dehydrogenation process, the sample was heated up to 200 °C in vacuum for more than 8 h until the peaks corresponding to $Mg(NH_2)_2$ and LiH disappeared. In the rehydrogenation, the dehydrogenated sample was kept at 200 °C under hydrogen atmospheres of 5 MPa and/or 1 MPa in several ten hours and/or 4 hours. After that, the sample was gradually cooled down to room temperature under 5 MPa H_2 for 24 h. We scanned the diffraction angle between 2θ(degrees) =10–65 with taking 30 min or 1 h for most of the measurement runs. The interval of each scan was set to 30 min or 1 h.

In this work, all the material handling was carried out in a glovebox filled with purified argon gas without exposing the sample to air except for the sample transfer to XRD equipment.

Result and discussion

1. Dehydrogenation process at 200 °C in vacuum

Figure 1 shows the in-situ XRD profiles during the dehydrogenation starting from (a) the mixture of 8LiH and $3Mg(NH_2)_2$ just after the ball milling and (b) the product after rehydrogenation at 200 °C under 5 MPa H_2 (after 1st cycle). In all XRD profiles, some minor peaks corresponding to Be, BeO (coming from the sample holder), LiCl (due to reaction between LiH and $TiCl_3$ dopant) and so on are observed. We consider these minor phases are not involved in the reactions as these peaks undergo no change during the measurement. The oxidation is small enough to be neglected in this experiment, since the oxide phases such as LiOH or Li_2O are not observed in all the profiles.

In Fig. 1(a), we notice that the composite mixture after ball milling shows only the weak LiH peak without containing any $Mg(NH_2)_2$ peaks. This indicates that the Mg amide in the composite prepared by ballmilling the mixture of LiH and $Mg(NH_2)_2$ is in an amorphous or nano-crystalline phase [23]. Even after heating up to 200 °C and desorbing hydrogen in vacuum, the Mg-related phase does not appear in the XRD profiles which might exist as amorphous or nano-structure [16], while the Li-related phase LiH seems to change into the Li_2NH phase.

After performing complete hydrogenation under 5 MPa H_2 at 200 °C for 37 h and then under slow cooling down to room temperature through 24 h, the crystallized Mg-related phase is observed as a tetragonal $Mg(NH_2)_2$ phase in addition to the cubic LiH phase. In the dehydrogenation process of the 2nd cycle at 200 °C in vacuum (see Figure 1(b)), the Li_2NH phase only grows up with increasing reaction time, while Mg-related phase or intermediate phase does not appear at all. As shown in Fig.1 (a) and (b), the peaks corresponding to $Mg(NH_2)_2$ and LiH disappear in the dehydrogenation process at 200 °C, indicating that the dehydrogenation almost proceeded. Therefore, it is expected that the Mg_3N_2 is produced by decomposition of $Mg(NH_2)_2$ in the dehydrogenation treatment at 200 °C in vacuum. Actually, 500 °C treatment in vacuum has successfully generated the Mg_3N_2 [16]. But, in the case of the 200 °C treatment, the crystalline size of Mg_3N_2 is not large enough to be detected by XRD, while a crystalline size of the Li_2NH is large enough to bear the specific XRD peaks.

Of course, we should take account of a possibility of bearing a new Mg-replaced Li_2NH single phase composed of Li_2NH and the Mg-related phase by heating at 200 °C in vacuum and growing up with increasing reaction time. Although it is quite difficult to judge which possibilities are correct, the detected profile shows a good agreement with the Li_2NH phase in the database (75-0050). Therefore, we have deduced that the Mg_3N_2 phase with nanometer size (nano-Mg_3N_2) was generated during the dehydrogenation of the Li-Mg-N-H system at 200 °C in vacuum.

Considering the above results, any intermediate phases such as MgNH or $LiNH_2$, which are expected from the ammonia mediating reaction model, do not appear in the XRD profile on the dehydrogenation process at 200 °C in vacuum. This result suggests two possibilities such that the crystalline size of intermediate phase is too small, or the reaction rate of intermediate step is too quick to be detected by our XRD experiments.

2. Rehydrogenation process under 5MPa at 200 °C

Next, we paid attention to the rehydrogenation process in the Li-Mg-N-H system. Figure 2 shows the in-situ XRD profiles in the (a) 1st and (b) 2nd hydrogenation processes under 5 MPa H_2 at 200 °C for the product after dehydrogenation at 200 °C in vacuum.

The interesting points are summarized as follows: (1) Both the overall XRD profiles in the 1st and 2nd hydrogenation processes are almost the same, indicating that the reversibility for the H-storage is suitable for applications. (2) The intensity of the Li_2NH phase peaks gradually decreases with increasing reaction time, while the peaks corresponding to the LiH and $Mg(NH_2)_2$ phases gradually grow up with increasing reaction time. (3) Any intermediate phases such as $LiNH_2$ or MgNH do not appear during the hydrogenation process at 200 °C under 5 MPa for 37 h. (4) A shoulder in the peak at 30° corresponding to the Li_2NH phase still remains even after rehydrogenation at 200 °C under 5 MPa H_2 for 37 h, indicating incomplete hydrogenation. (5) However, after that, the hydrogenation completely progresses with slow cooling down to room temperature under 5 MPa H_2 atmospheres from 200 °C for 24 h because the shoulder at 30° disappears at room temperature after cooling down.

Because we have known that the Mg_3N_2 phase could not be hydrogenated under this trial condition, the appearance of the $Mg(NH_2)_2$ implies the existence of some intermediate phases. However, the above results did not show any intermediate phases. Therefore, it seems that the crystalline size of intermediate phase is too small, or the reaction rate of intermediate step is too quick to be detected by our XRD experiments, irrespective of the hydrogenation and dehydrogenation processes.

3. Hydrogenation under 1MPa at 200 °C

Finally, we tried to observe the hydrogenation process under a lower H_2 pressure of 1 MPa at 200 °C to check whether any intermediate phases appear or not. Here, it is noteworthy that the operating pressure of 1MPa H_2 corresponds to the first hydrogenation step in the PCI curve [20]. It is quite obvious that the second hydrogenation step in the PCI curve leads to the final product of LiH and $Mg(NH_2)_2$. However, it is obscure which kind of phases appear in the product after the first step of hydrogenation. The results of the in-situ XRD profiles for the Li-Mg-N-H system in the hydrogenation process under 1MPa H_2 at 200 °C are shown in Figure 3. We notice that the $LiNH_2$ phase appears and grows up with increasing reaction time without appearance of the $Mg(NH_2)_2$ phase. Although a peak at 30° seems to be due to the existence of $Mg(NH_2)_2$, this peak should not be the origin of $Mg(NH_2)_2$ because the other $Mg(NH_2)_2$ peaks can't be recognized. As the diffraction peaks of the LiH phase is superposed with the $Mg(NH_2)_2$ peaks at 38° and with the Be, BeO peaks (coming from the sample holder) at 43°, it is quite difficult to confirm whether the LiH phase exists or not in the XRD profiles. However, we notice that the peaks around 38° without growth of other $Mg(NH_2)_2$ peaks and around 43° grow up with increasing reaction time, suggesting that LiH also grows up during the hydrogenation at 200 °C under 1 MPa.

Considering the above results, we conclude that $LiNH_2$ exists as an intermediate phase in the hydrogenation process under 1 MPa H_2 at 200 °C without appearance of any Mg-related phases in our experimental accuracy. Perhaps, the crystallites of the Mg-related phases are in several nanometer sizes. More detailed studies are necessary.

The appearance of $LiNH_2$ suggests that the composite of Li_2NH and nano-Mg_3N_2 phases are transformed into LiH and $Mg(NH_2)_2$ through the intermediate $LiNH_2$ phase by hydrogenation at 200 °C as follows:

$$4Li_2NH + 4\,H_2 \rightarrow 4LiNH_2 + 4LiH \quad (6)$$

$$4LiNH_2 + 1/2Mg_3N_2 \rightarrow 2Li_2NH + 2NH_3 + 1/2Mg_3N_2$$

$$\rightarrow 2Li_2NH + 2/3Mg(NH_2)_2 \quad (7).$$

The hydrogenation at 200 °C under 1 MPa H_2 indicates that the reaction (6) proceeds as a 1st step reaction in the low pressure phase because the $LiNH_2$ and LiH phases have been observed in the XRD profiles. Furthermore, the hydrogenation at 200 °C under 5 MPa bears the LiH and $Mg(NH_2)_2$ phases, indicating that the equilibrium pressure of reaction (7) is higher than 5 MPa at 200 °C. In conclusion, the $LiNH_2$ phase is observed as the intermediate state during the hydrogenation of the Li-Mg-N-H system. From this result, it is clarified that the hydrogenation of the Li-Mg-N-H system is only understood by the ammonia mediating model [21] expressed in the reactions (6) and (7).

Summary

In this work, the dehydrogenation and rehydrogenation processes of the Li-Mg-N-H system composed of 8LiH and $Mg(NH_2)_2$ were examined by the in-situ XRD measurements. The results obtained are summarized as follows:

(1) In the dehydrogenation process at 200 °C in vacuum, the mixed phase of 8LiH and $Mg(NH_2)_2$ gradually changed into the Li_2NH phase without any traces corresponding to Mg-related phases.

(2) In the rehydrogenation process at 200 °C under 5 MPa after releasing hydrogen at 200 °C, the $Mg(NH_2)_2$ and LiH phases gradually grow up with increasing reaction time. However, any traces corresponding to the Mg-related phases or intermediate phases such as MgNH or $LiNH_2$ could not be detected in the profile.

(3) In the rehydrogenation process at 200 °C under 1 MPa after releasing hydrogen at 200 °C, the $LiNH_2$ phase appears and grows up with increasing reaction time without appearance of the $Mg(NH_2)_2$ phase.

(4) Especially, no diffraction peak corresponding to intermediate phases were detected in the dehydrogenation process and the rehydrogenation process under

5MPa H_2. These results suggest two possibilities such that the crystalline size of intermediate phase is too small, or the reaction rate of intermediate step is too quick to be detected by our XRD experiment.

(5) However, we can suggest that the $LiNH_2$ phase essentially appears as an intermediate state in the Li-Mg-N-H system composed of $3Mg(NH_2)_2$ and 8LiH, since $LiNH_2$ was observed at 200 °C under 1 MPa.

Acknowledgments

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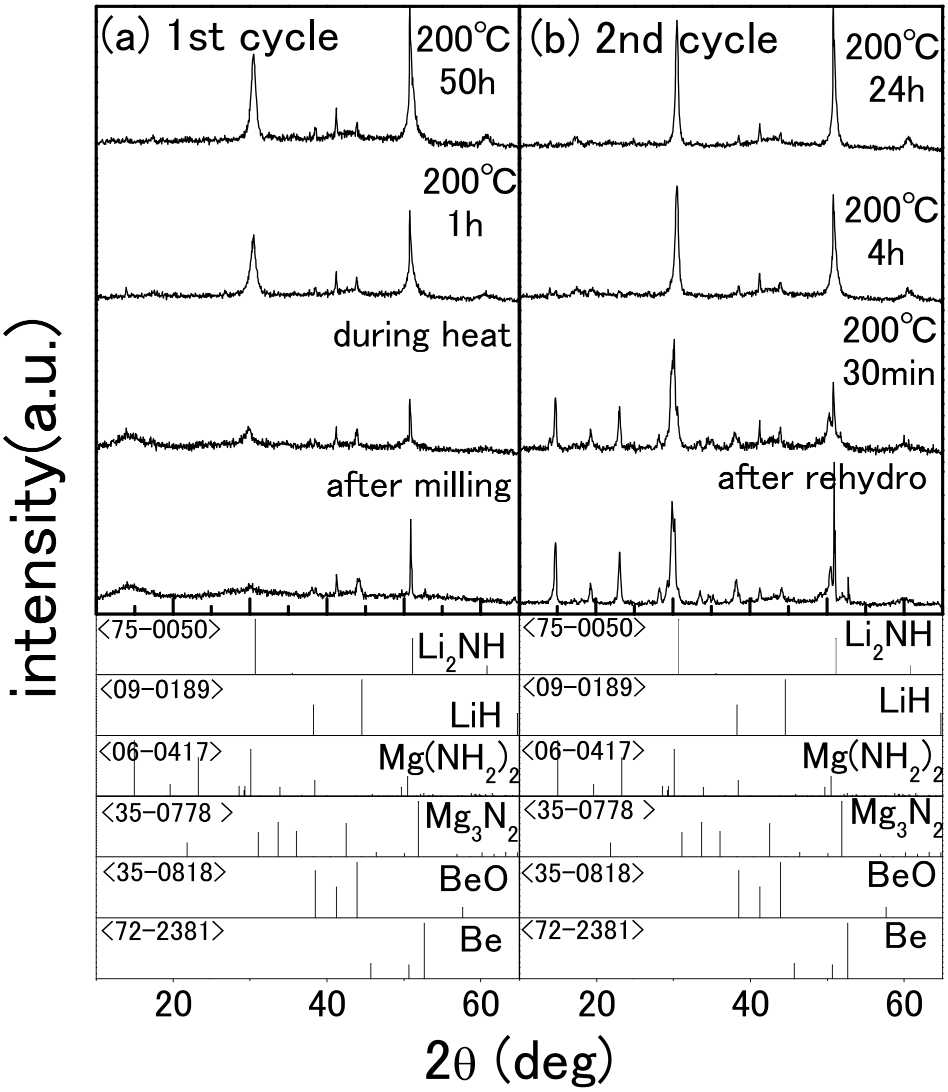

Figure 1. XRD profiles in the dehydrogenation process for the ballmilled 8LiH and $3Mg(NH_2)_2$ mixture at first cycle (a) and second cycle (b) under vacuum condition.

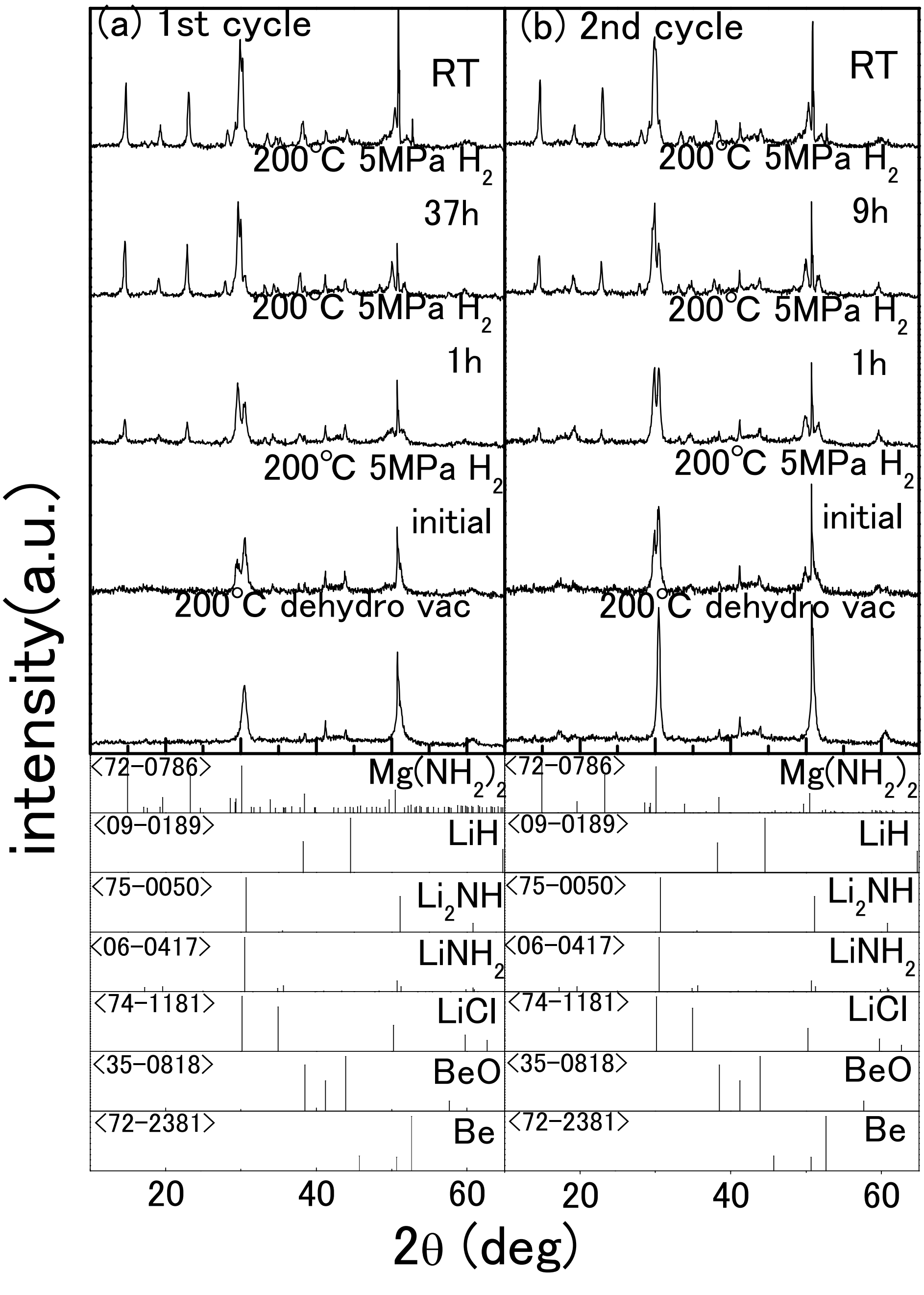

Figure 2. XRD profiles in the rehydrogenation process in 5MPa H_2 after the dehydrogenation of the 8LiH and $3Mg(NH_2)_2$ mixture at first cycle (a) and second cycle (b). The "initial" profiles stand for the measurements just after introducing hydrogen.

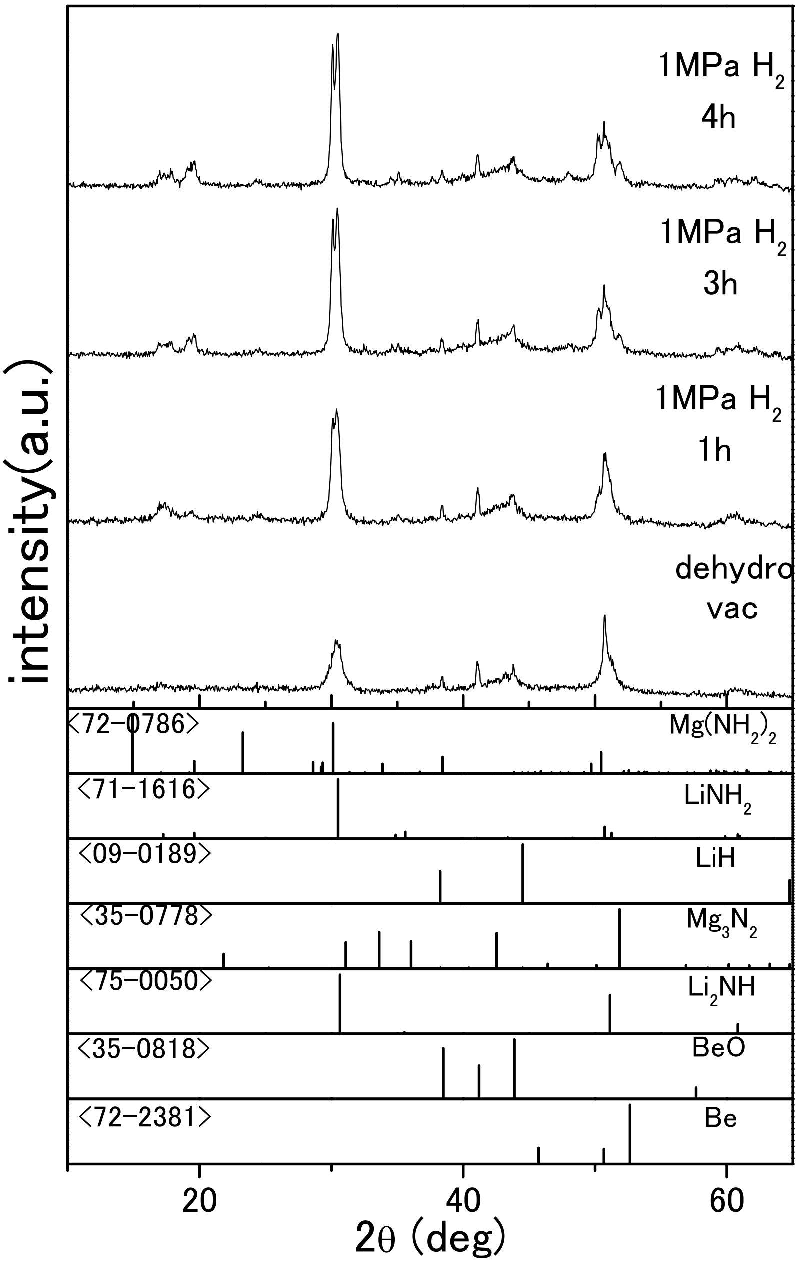

Figure 3. X-ray diffraction profiles in the rehydrogenation process under 1MPa H_2 after the dehydrogenation of the 8LiH and $3Mg(NH_2)_2$ mixture at 200 °C.