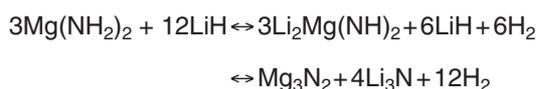


Development of Hydrogen Storage Materials by Crystal Structure Analysis of Light Element Hydrides

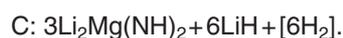
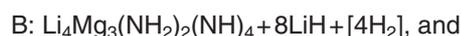
Hydrogen storage is one of the key technologies that should be developed to utilize hydrogen as a clean energy source. The development of safe and efficient hydrogen storage materials is indispensable for the popularization of fuel-cell vehicles. Thus, hydrogen storage alloys have been mainly investigated, but the gravimetric hydrogen density of these alloys is lower than 3 mass%. In recent years, complex hydrides that consist of light elements, such as LiBH_4 and LiNH_2 , have attracted considerable attention as new hydrogen storage materials [1] because of their high gravimetric hydrogen density (LiBH_4 : 18.5 mass%; LiNH_2 : 8.8 mass%). Generally, these complex hydrides release hydrogen by thermal decomposition reaction but cannot absorb hydrogen. Namely, the reversible hydrogen storage reaction in these complex hydrides is difficult. However, it has recently been reported that reversible hydrogen storage is possible in a NaAlH_4 system with a Ti catalyst and in a $\text{LiNH}_2 + \text{LiH}$ mixture system. Furthermore, it was found that the mixture of $\text{Mg}_3\text{N}_2 + 4\text{Li}_3\text{N}$ exhibits reversible hydrogen storage functions in which hydrogen of 9.1 mass% density of can be stored [2,3]. In this system, intermediate phases, such as $\text{Li}_2\text{Mg}(\text{NH})_2$, are created in the reaction process according to the following formula:



It is expected that the intermediate phases will be important in the reversible reaction. However, the intermediate phases are novel hydrides and their structures are unknown. As a result, the reversible reaction mechanism has not yet been clarified. Therefore, these crystal structure analyses have been performed in order to understand the reaction mechanism. The diffraction intensities from hydrogen and lithium atoms are very low; thus, the highly brilliant X-ray source at beamline **BL19B2** was used for the diffraction measurement.

The mixture of $\text{Mg}_3\text{N}_2 + 4\text{Li}_3\text{N}$ was prepared by ball milling. First, the mixture was hydrogenated at a hydrogen pressure of 9.5 MPa, and then pressure-composition (p-c) isotherm measurement during the dehydrogenation process was performed at 523 K using the conventional Sieverts apparatus [4]. At several dehydrogenation stages of p-c isotherm measurement, the sample was taken out and the X-ray powder diffraction was measured. The

crystal structure was analyzed by the Rietveld method using the computer program RIETAN. The result of p-c isotherm measurement and the sampling points are shown in Fig. 1. At the sampling points A, B and C, the hydrogen pressures (and the amounts of hydrogen desorption) are 9.5 MPa (0.0 mass%), 6.0 MPa (3.1 mass%) and 0.06 MPa (4.9 mass%), respectively. According to the amount of hydrogen desorbed during the p-c isotherm measurement, the following chemical formulas of samples A, B and C were estimated:



The analyzed crystal structures of $\text{Mg}(\text{NH}_2)_2$, $\text{Li}_4\text{Mg}_3(\text{NH}_2)_2(\text{NH})_4$ and $\text{Li}_2\text{Mg}(\text{NH})_2$ are shown in Fig. 2. These crystal structures are similar to those of the anti- CaF_2 type. Namely, anions ($\{\text{NH}_2\}^-$ or $\{\text{NH}\}^{2-}$) are in the FCC-type arrangement and cations

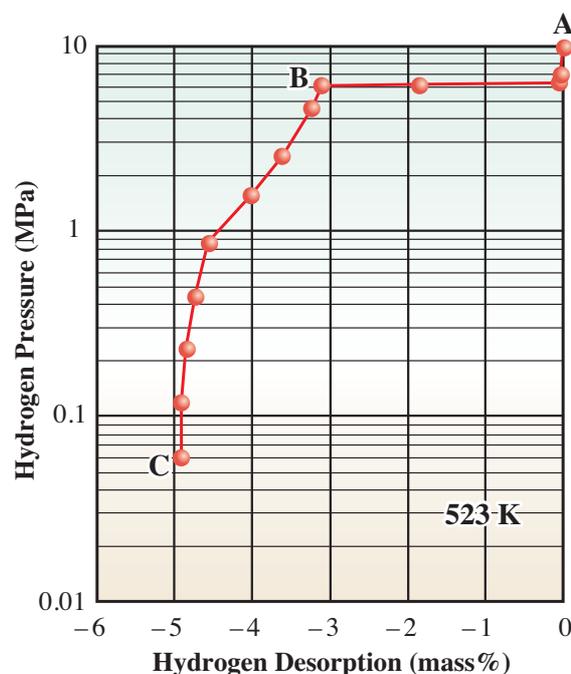


Fig. 1. p-c isotherm during dehydrogenation of $\text{Mg}_3\text{N}_2 + 4\text{Li}_3\text{N}$ mixture at 523 K after hydrogenation. A, B and C indicate the sampling points for the X-ray measurement.

(Mg²⁺ and Li⁺) are located at eight interstitial sites. Nitrogen atoms coordinate at tetrahedral sites around cations. In Mg(NH₂)₂, Mg²⁺ ions are located at two cation sites and the other six cation sites are vacant. In Li₄Mg₃(NH₂)₂(NH)₄ and Li₂Mg(NH)₂ formed during the dehydrogenation process, Mg²⁺ and Li⁺ ions are randomly distributed among the cation sites. Consequently, the cation sites are Mg-rich, Li-rich or vacant according to the chemical composition [5].

As a result of this structure analysis, it is considered that the dehydrogenation reaction is related to the diffusion of Li⁺ ions at cation sites of Mg(NH₂)₂. Namely, Li⁺ ions diffuse from LiH to Mg(NH₂)₂ crystal and then decompose {NH₂}⁻ into {NH}²⁻ and H⁺. The created H⁺ ions in Mg(NH₂)₂ attach to the side of LiH and combine with H⁻. Consequently, H₂ gas is released. Hydrogenation is induced probably by the reverse process, which begins with the dissociation of a hydrogen molecule. The dehydrogenation of the Mg(NH₂)₂+LiH system is illustrated in Fig. 3. Furthermore, it has been clarified that the reversibility of the hydrogenation and dehydrogenation reaction of the Mg(NH₂)₂+LiH system is caused by the similarity in the structures of imides and amides. In the future, the development of catalysts or additives that enhance the diffusion of Li⁺ ions will be necessary for practical use. Crystal structure analysis will be important in future research of new hydrogen storage materials.

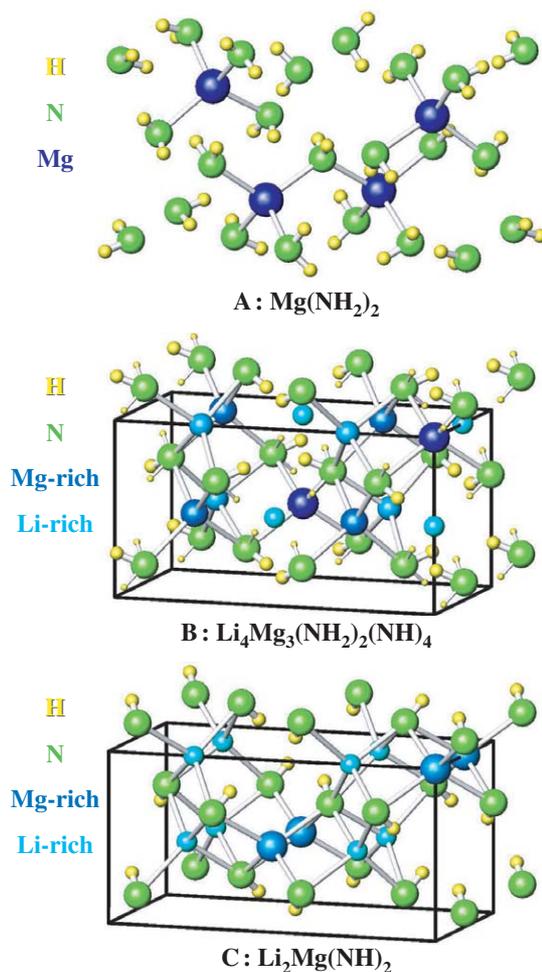


Fig. 2. Crystal structures of Mg(NH₂)₂, Li₄Mg₃(NH₂)₂(NH)₄ and Li₂Mg(NH)₂. The small light blue and large dark blue spheres represent the Li-rich and Mg-rich sites, respectively.

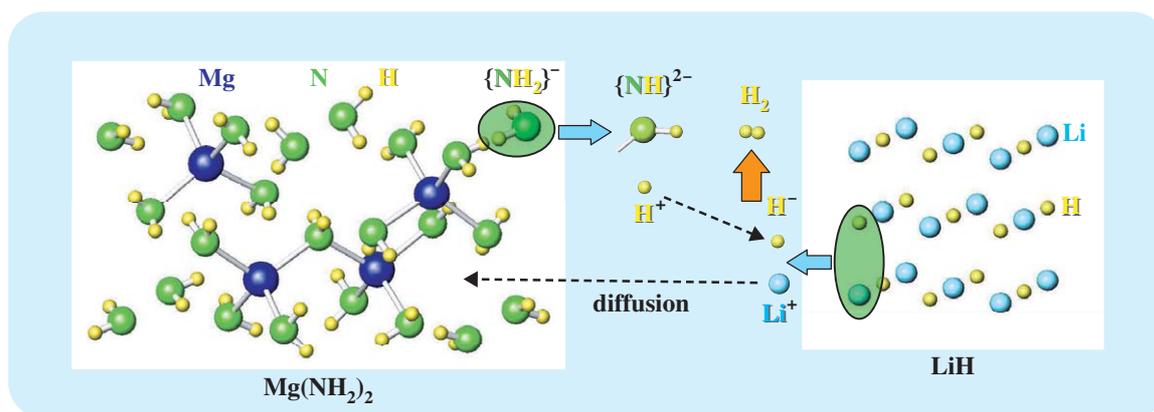


Fig. 3. Illustration of dehydrogenation of Mg(NH₂)₂+LiH system.

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