

Formation of Intermediate Compound $\text{Li}_2\text{B}_{12}\text{H}_{12}$ during the Dehydrogenation Process of the $\text{LiBH}_4\text{--MgH}_2$ System

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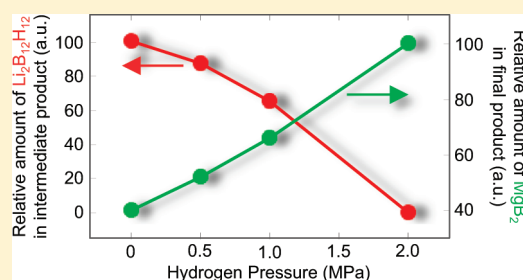
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S Supporting Information

ABSTRACT: Intermediate compound comprising $[\text{B}_{12}\text{H}_{12}]^{2-}$ anion formed in the dehydrogenation is regarded to be responsible for the degradation of reversibility of metal borohydrides, whereas little is known about the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ in the $\text{LiBH}_4\text{--MgH}_2$ combined system. In this study, we investigated the dehydrogenation process of the $\text{LiBH}_4\text{--MgH}_2$ system in a heating run under different hydrogen pressures. Our experimental results demonstrated, for the first time, that $\text{Li}_2\text{B}_{12}\text{H}_{12}$ was formed under hydrogen pressure ≤ 1.0 MPa, but not formed under 2.0 MPa. Moreover, the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ was found to negatively depending on the hydrogen pressure, and also influence subsequent formation of MgB_2 : the more $\text{Li}_2\text{B}_{12}\text{H}_{12}$ that formed, the less MgB_2 obtained. These findings indicate that suppression of the formation of intermediate compound $\text{Li}_2\text{B}_{12}\text{H}_{12}$, such as by using adequate hydrogen pressures (e.g., 2.0 MPa), is of great importance for further improvement of hydrogen storage properties of the $\text{LiBH}_4\text{--MgH}_2$ system.



INTRODUCTION

Metal borohydride $\text{M}(\text{BH}_4)_n$ (n indicates the valence of metal M) have been attracting significant interest as the potential candidates for hydrogen storage materials because of their high hydrogen densities.^{1,2} Most of them, however, suffer from their high dehydrogenation temperatures. Toward reducing such high temperatures, extensive efforts have been mainly focused on three strategies: novel additives,^{3,4} confinement into nanoporous materials,^{5–8} and combined systems with metal or metal hydride.^{9–19} Among these strategies, combined systems proved to effectively adjust the reaction enthalpy.

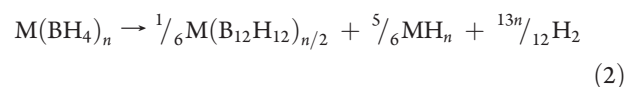
A typical example is the $\text{LiBH}_4\text{--MgH}_2$ system demonstrated first by Vajo et al.,⁹ in which a 11.4 mass % reversible storage capacity has been achieved via reaction 1.



Reaction 1 was reported to proceed in two steps: MgH_2 first dehydrogenates into Mg , which subsequently reacts with LiBH_4 to form LiH and MgB_2 .^{13–15} The formation of MgB_2 , which is considered to be crucial for the reversibility of reaction 1, however, largely depends on hydrogen pressures.^{13–15,20–22} For example, a hydrogen pressure of at least 0.3 MPa is required to suppress the individual decomposition of LiBH_4 before the occurrence of reaction 1 to produce LiH and MgB_2 . Similar influence

of hydrogen pressures on formation of borides are also observed in $\text{LiBH}_4\text{--YH}_3$, $\text{LiBH}_4\text{--CeH}_2$, and $\text{LiBH}_4\text{--CaH}_2$ systems.²³

As for single systems of $\text{M}(\text{BH}_4)_n$ dehydrogenation reactions are thermodynamically favorable to proceed via the formation of intermediate compounds $\text{M}(\text{B}_{12}\text{H}_{12})_{n/2}$ according to the following reaction:^{24–30}



The intermediate compound $\text{M}(\text{B}_{12}\text{H}_{12})_{n/2}$ is quite stable, which was reported to degrade or hinder the rehydrogenation reaction of $\text{M}(\text{BH}_4)_n$.^{30–32}

Recent theoretical calculations predict $\text{Li}_2\text{B}_{12}\text{H}_{12}$ as a thermodynamically favorable intermediate compound during the dehydrogenation reaction of $\text{LiBH}_4\text{--MgH}_2$.³³ The possible formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and its influence on the formation of MgB_2 under different hydrogen pressures are of great importance to be clarified for further development of the $\text{LiBH}_4\text{--MgH}_2$ system.

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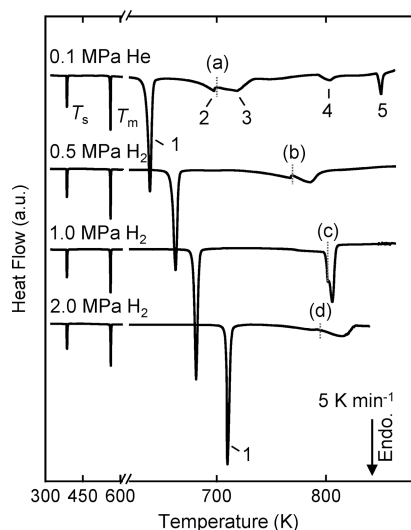


Figure 1. PDSC curves of $2\text{LiBH}_4 + \text{MgH}_2$ under 0.1 MPa of He and 0.5, 1.0, and 2.0 MPa of H_2 at a heating rate of 5 K min^{-1} . T_s and T_m represent the structural transformation and melting of LiBH_4 . The intermediate dehydrogenation products at conditions of (a)–(d) are examined by XRD, Raman spectroscopy, and ^{11}B MAS NMR measurements, as shown in Figure 2, Figure 3, and Figure 4, respectively.

In present research, we experimentally investigate the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ during the dehydrogenation process of the $\text{LiBH}_4\text{--MgH}_2$ system under different hydrogen pressures by using powder X-ray diffraction (XRD), Raman spectroscopy, and ^{11}B MAS NMR measurements. The possible influence of the intermediate compound $\text{Li}_2\text{B}_{12}\text{H}_{12}$ on the subsequent formation of MgB_2 is further discussed. This study sheds light on the understanding of the reaction mechanism and further improvement of hydrogen storage properties of the $\text{LiBH}_4\text{--MgH}_2$ system, and also other metal borohydride related systems.

EXPERIMENTAL SECTION

The starting materials of LiBH_4 (purity, 95%) and MgH_2 (purity, 98%) were purchased from Sigma-Aldrich Corp. The sample of $2\text{LiBH}_4 + \text{MgH}_2$ was prepared by mechanical milling (Fritsch P-7, 400 rpm, ball to powder ratio of 20:1) in a hardened steel vial (30 cm^3 in volume) under 0.1 MPa Ar. The sample after ball milling (as-BM) is a physical mixture of LiBH_4 and MgH_2 as examined by XRD measurement (Figure S1). The dehydrogenation reactions were carried out by using a pressure differential scanning calorimetry (PDSC) apparatus (TA INSTRUMENTS DSC Q10; range, 0–7.0 MPa hydrogen; heat rate, 5 K min^{-1} ; flow rate, 200 mL min^{-1}) placed inside a glove box under purified, circulated helium. A carbon steel sample pan is used in the thermal analysis measurement.

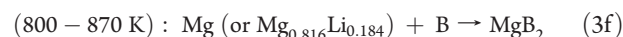
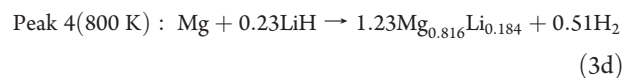
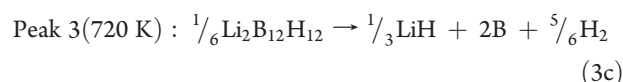
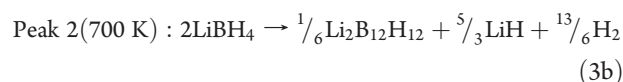
To elucidate the formation of the intermediate compound $\text{Li}_2\text{B}_{12}\text{H}_{12}$, the as-prepared sample was partly decomposed by heating up to different assigned temperatures under different pressures, followed by rapid quenching to room temperature. The obtained dehydrogenation samples were characterized by XRD (PANalytical X'PERT with $\text{Cu K}\alpha$ radiation) and Raman spectroscopy (Nicolet, Almega-HD) at room temperature. The chemical bonding states of boron atoms were further investigated via ^{11}B MAS NMR measurement at room temperature (JEOL Ltd., JNM-ECA600 spectrometer operated at a magnetic field of 14.1 T; resonance frequency, 192.57 MHz; spinning rate of 4.0 mmφ sample rotor, 16 kHz). Spectra were obtained by using a

single pulse sequence with the pulse width of $1 \mu\text{s}$, which was set equivalent to a $\pi/9$ of the solution $\pi/2$ pulse. For each spectrum, 6000 scans were accumulated with a repetition time of 2 s. The chemical shift (in ppm) was determined using a $\text{BF}_3(\text{Et}_2\text{O})$ in ether solution as reference. Throughout the study, the samples were manipulated in a glove box filled with purified Ar/He gas (dew point, $< 183 \text{ K}$; oxygen concentration, $< 1 \text{ ppm}$) in order to prevent (hydro-) oxidation.

RESULTS AND DISCUSSION

Figure 1 shows the PDSC curves of $2\text{LiBH}_4 + \text{MgH}_2$ under different pressures. The two peaks at 380 and 550 K in all PDSC curves correspond to the structural transformation and melting of LiBH_4 ,²⁴ respectively.

Under 0.1 MPa of He, five endothermic peaks are observed at temperatures above 600 K, as denoted by numbers of 1–5 in Figure 1. XRD profiles and Raman spectra of the dehydrogenation products heated to temperatures above each peak are shown in Figures S1 and S2 (Supporting Information). On the basis of these experimental results, the dehydrogenation pathway of $2\text{LiBH}_4 + \text{MgH}_2$ under 0.1 MPa of He can be expressed as the following equations:



Under this condition, MgH_2 and LiBH_4 decompose individually according to eqs 3a and 3b, respectively, as shown in Figure 1. In addition, the formation of a small amount of MgB_2 at temperatures ranging from 800 to 870 K are mainly attributed to the reaction between Mg or $\text{Mg}_{0.816}\text{Li}_{0.184}$ and boron (a dehydrogenation product of LiBH_4), as expressed by eq 3f.

As the hydrogen pressure increases, Peak 1 ($\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$) shifts to the higher temperature side according to the van't Hoff equation (Figure 1); and the subsequent reaction between the formed Mg and LiBH_4 is observed to occur in two steps under 0.5–1.0 MPa of H_2 and nearly one step under 2.0 MPa of H_2 . These findings clearly show that the dehydrogenation pathway of $2\text{LiBH}_4 + \text{MgH}_2$ strongly depends on hydrogen pressure. To elucidate this dependence, the intermediate dehydrogenation products at conditions of (a)–(d) in Figure 1 were examined by XRD (Figure 2), Raman spectroscopy (Figure 3), and ^{11}B MAS NMR measurements (Figure 4).

In the XRD profiles (Figure 2), the phases of Mg obtained from Peak 1 ($\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$) and the undecomposed LiBH_4 are identified for all the intermediate dehydrogenation products. MgH_2 results from the reaction of Mg with H_2 during the cooling process. The formation of MgB_2 is only observed at conditions of (c) and (d) with hydrogen pressure $\geq 1.0 \text{ MPa}$.

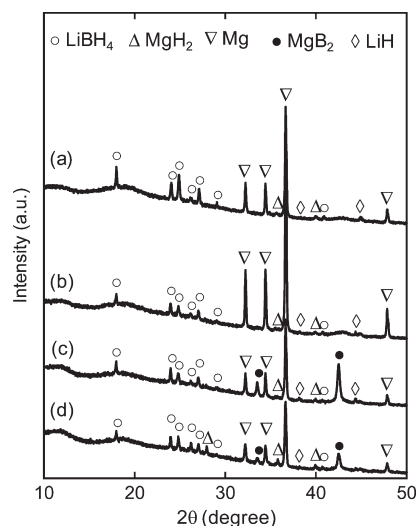


Figure 2. XRD profiles of the intermediate dehydrogenation products at conditions of (a)–(d) in Figure 1. (a) 700 K, 0.1 MPa He, (b) 770 K, 0.5 MPa H₂, (c) 802 K, 1.0 MPa H₂, and (d) 798 K, 2.0 MPa H₂.

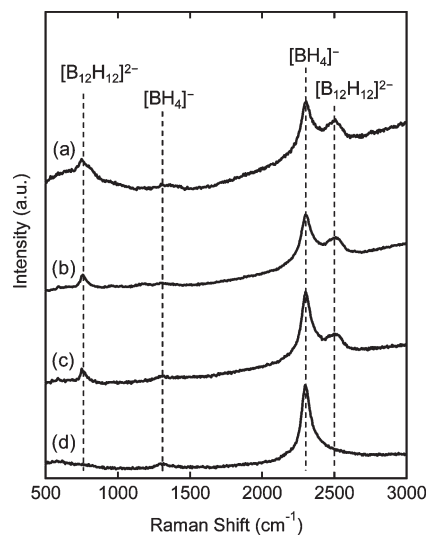


Figure 3. Raman spectra of the intermediate dehydrogenation products at conditions of (a)–(d) in Figure 1.

In Raman spectra (Figure 3), the vibration modes of $[\text{B}_{12}\text{H}_{12}]^{2-}$ anion at 750 and 2500 cm^{-1} are detected at (a)–(c) when hydrogen pressure ≤ 1.0 MPa, while not observed at (d) under 2.0 MPa of H₂. The formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and MgB_2 at hydrogen pressures of 0.5 and 2.0 MPa, respectively, is also confirmed by ^{11}B MAS NMR measurement (Figure 4). These findings indicate that the intermediate compound $\text{Li}_2\text{B}_{12}\text{H}_{12}$ is formed from the individual decomposition of LiBH_4 (eq 3b), when hydrogen pressure ≤ 1.0 MPa. At a hydrogen pressure of 2.0 MPa, the individual decomposition of LiBH_4 is suppressed, which facilitates the formation of MgB_2 according to eq 4.



The XRD profiles of the final dehydrogenation products under different hydrogen pressures are shown in Figure 5. The formation of LiH and MgB_2 are confirmed in all the samples.

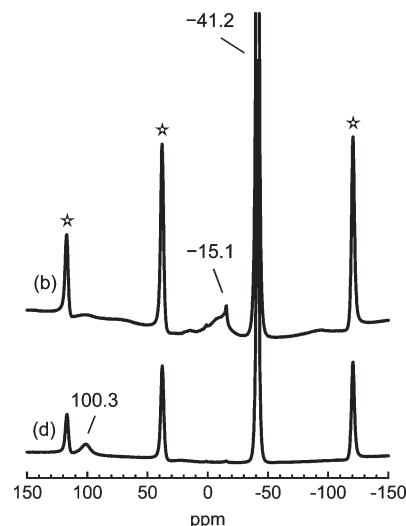


Figure 4. ^{11}B MAS NMR spectra of the intermediate dehydrogenation products at conditions of (b) and (d) in Figure 1. Peaks at -41.2 , -15.1 , and 100.3 ppm are assigned to LiBH_4 ,²⁸ $\text{Li}_2\text{B}_{12}\text{H}_{12}$,^{28,34} and MgB_2 ,³⁵ respectively. The stars represent the side bands of LiBH_4 , respectively.

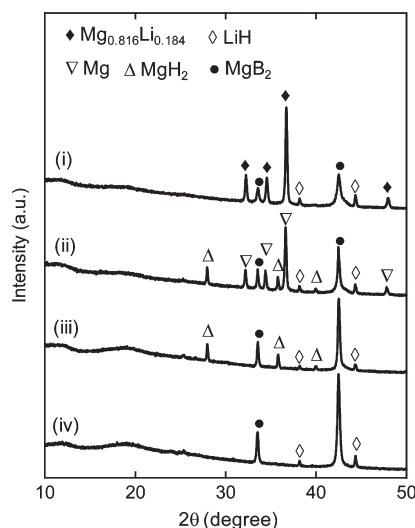


Figure 5. XRD profiles of final dehydrogenation products of $2\text{LiBH}_4 + \text{MgH}_2$ at (i) 863 K, 0.1 MPa He, (ii) 810 K, 0.5 MPa H₂, (iii) 820 K, 1.0 MPa H₂, and (iv) 830 K, 2.0 MPa H₂.

The increase of diffraction peak intensities of MgB_2 with hydrogen pressures proves that higher hydrogen pressure facilitates the formation of MgB_2 . The remaining Mg ($\text{Mg}_{0.816}\text{Li}_{0.184}$ or MgH_2) at hydrogen pressures ≤ 1.0 MPa obviously indicates the reaction between Mg with LiBH_4 to produce MgB_2 is not completed and influenced by the appearance of $\text{Li}_2\text{B}_{12}\text{H}_{12}$.

A relationship between the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and MgB_2 is revealed in Figure 6. With increasing the hydrogen pressure, the relative amount of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ decreases, whereas that of MgB_2 increases. In other words, at hydrogen pressures ≤ 1.0 MPa, the appearance of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ hinders the formation of MgB_2 . This can be explained as follows. First, at hydrogen pressures ≤ 1.0 MPa, LiBH_4 tends to decompose individually and thus produces $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (Figure 3), whereas higher hydrogen pressures express better suppression effect on the individual decomposition of

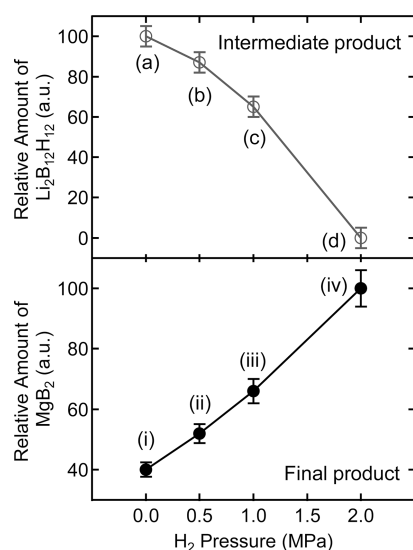


Figure 6. Relationship between the formation of the intermediate compound $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and final product of MgB_2 under different pressure; He atmosphere is regarded as a hydrogen pressure of 0 MPa. The relative amounts of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and MgB_2 are roughly calculated from Raman spectra area of (a)–(d) in Figure 3 and diffraction peak area of (i)–(iv) in Figure 5, respectively; the calculation method is shown in the Supporting Information.

LiBH_4 from the viewpoint of chemical equilibrium. Second, the reaction between $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and Mg is restricted by a high kinetic barrier. It was reported that no new phase was observed when the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ – MgH_2 (molar ratio of 1:6) system was dehydrogenated at 673 K,³⁶ possibly due to the high stability of $[\text{B}_{12}\text{H}_{12}]^{2-}$ icosahedral units.²⁵ Third, $\text{Li}_2\text{B}_{12}\text{H}_{12}$ would block the contact between LiBH_4 and Mg, and thus hinder the formation reaction of MgB_2 ; a similar case has been reported in the LiBH_4 – YH_3 system.²³ Therefore, suppressing the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ from the individual decomposition of LiBH_4 (eq 3b), such as using adequate hydrogen pressures (e.g., 2.0 MPa) higher than the equilibrium pressure for the decomposition of LiBH_4 , is quite important for producing MgB_2 according to eq 4.

Further study on the suppression of $\text{M}(\text{B}_{12}\text{H}_{12})_{n/2}$ is also highly expected for the improvement of reversible hydrogen storage properties in the single $\text{M}(\text{BH}_4)_n$ systems. We are currently investigating the formation mechanism of $\text{M}(\text{B}_{12}\text{H}_{12})_{n/2}$ toward developing effective ways to suppress its formation.

CONCLUSIONS

The formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ as an intermediate compound during the dehydrogenation process of the LiBH_4 – MgH_2 system has been experimentally investigated under different hydrogen pressures. Raman and ^{11}B MAS NMR spectra consistently indicate the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ under hydrogen pressure ≤ 1.0 MPa. With increasing hydrogen pressure, the relative amount of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ decreases, whereas that of MgB_2 increases. Suppression of the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ from the individual decomposition of LiBH_4 , such as by using adequate hydrogen pressures (e.g., 2.0 MPa), facilitates the formation of MgB_2 from the reaction between LiBH_4 and Mg. Further studies on the development of effective ways to suppress the formation of $\text{M}(\text{B}_{12}\text{H}_{12})_{n/2}$ are one of important issues for designing $\text{M}(\text{BH}_4)_n$ related systems with good reversibility.

ASSOCIATED CONTENT

S Supporting Information. Figure S1 shows (a) XRD profiles of the $2\text{LiBH}_4 + \text{MgH}_2$ sample heated to different temperatures and (b) enlarged XRD profiles of (a) for detailed peak identification. Figure S2 shows the Raman spectra of the $2\text{LiBH}_4 + \text{MgH}_2$ sample. This material is available free of charge via the Internet at <http://pubs.acs.org>

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