

Experimental studies on intermediate compound of LiBH_4

Shin-Ichi Orimo^{a)} and Yuko Nakamori

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Nobuko Ohba, Kazutoshi Miwa, Masakazu Aoki, and Shin-ichi Towata

Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan

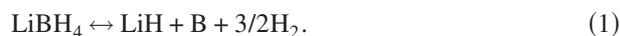
Andreas Züttel

Physics Department, University of Fribourg, Perolles 1700, Switzerland and Department of Environment, Energy and Mobility, EMPA, Dübendorf, 8600, Switzerland

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The formation condition of an intermediate compound of LiBH_4 during the partial dehydriding reaction and its local atomistic structure have been experimentally investigated. LiBH_4 changes into an intermediate compound accompanying the release of approximately 11 mass % of hydrogen at 700–730 K. The Raman spectra indicate that the B–H bending and stretching modes of the compound appear at lower and higher frequencies, respectively, as compared to those of LiBH_4 . These features are consistent with the theoretical calculation on the monoclinic $\text{Li}_2\text{B}_{12}\text{H}_{12}$, consisting of Li^+ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ ions, as a possible intermediate compound of LiBH_4 . © 2006 American Institute of Physics. [DOI: 10.1063/1.2221880]

Experimental and theoretical researches on complex hydrides are of great importance to develop advanced hydrogen storage materials,^{1,2} and LiBH_4 is a potential candidate for the material.^{3,4} Dehydriding reaction of LiBH_4 accompanied by the phase decomposition has been expressed as the reaction of left-to-right direction in the following overall equation:

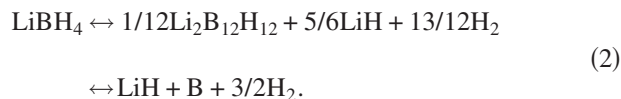


During the dehydriding (decomposition) reaction, 13.8 mass % of hydrogen can be released,^{3–5} and the amount is sufficient for applying LiBH_4 to the hydrogen storage material (required amount >6 mass %).^{1,2} However, the enthalpy change in Eq. (1) is theoretically estimated to be 75 kJ/mol H_2 ,⁵ indicating too stable to proceed the dehydriding reaction at ambient condition.

So far, we have reported that appropriate elemental substitutions or microwave irradiations resulted in promoting the dehydriding reaction,^{6–8} and also that the dehydrided (decomposed) LiBH_4 , namely, a mixture of LiH and B, was reversibly rehydrided (recombined) into LiBH_4 under 35 MPa of hydrogen at 873 K.⁶ Züttel *et al.* have pointed out that the thermal desorption profile of LiBH_4 mixed with SiO_2 powder exhibited the multisteps dehydriding reaction, implying the formation of the intermediate compound of LiBH_4 .³ Also, Kang *et al.* have theoretically investigated the possibility of the dehydriding reaction via LiBH as an intermediate compound.⁹ Judging from the reports, the dehydriding and/or the reversible reactions of LiBH_4 at ambient condition are expected to proceed by using appropriate intermediate compounds, similar to the other complex hydrides such as NaAlH_4 ^{10–17} and LiNH_2 .^{18–20}

By the first-principles calculation, Ohba *et al.* have just recently reported the stability of the candidates of the intermediate compounds of LiBH_4 ; LiB_3H_8 and $\text{Li}_2\text{B}_n\text{H}_n$ ($n=5–12$).²¹ The computational results provide that the monoclinic $\text{Li}_2\text{B}_{12}\text{H}_{12}$ is the most stable one (an insulator

with the energy gap of 5.6 eV) among the candidates, and $\text{Li}_2\text{B}_{12}\text{H}_{12}$ consists of Li^+ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ ions, as shown in Fig. 1. Assuming a dehydriding reaction via $\text{Li}_2\text{B}_{12}\text{H}_{12}$, the following equation of LiBH_4 is proposed:



The dehydriding amounts in the first- and second-step reactions are calculated to be approximately 10 and 4 mass %, respectively. Moreover, the enthalpy change of the first-step reaction in Eq. (2), 56 kJ/mol H_2 , is approximately 20 kJ/mol H_2 smaller than that of the reaction in Eq. (1). Although it might be interesting to effectively use the first-step reaction in Eq. (2) for promoting the reactions of LiBH_4 at ambient condition, there is little experimental information about the intermediate compound.

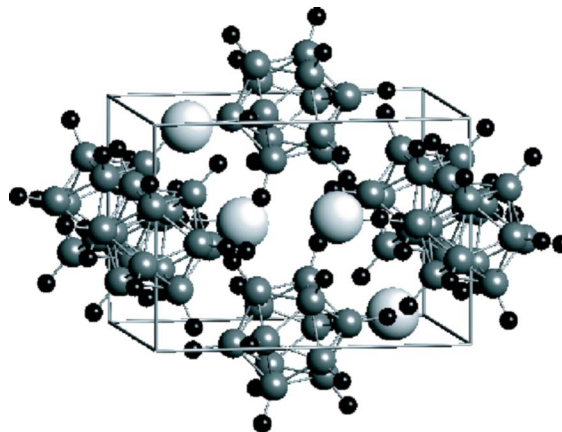


FIG. 1. Atomistic structure model of the monoclinic $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (space group: $P2_1/n$, $Z=2$; $a=7.358$ Å, $b=9.556$ Å, $c=6.768$ Å, $\beta=92.26^\circ$; from Ref. 21). The large, middle, and small spheres denote Li, B, and H atoms, respectively.

^{a)}Electronic mail: orimo@imr.tohoku.ac.jp

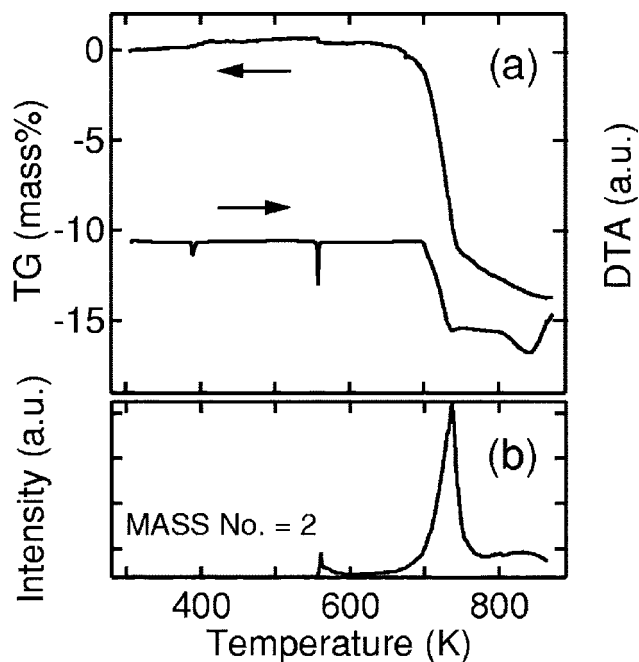


FIG. 2. (a) Thermogravimetry (TG) and differential thermal analysis (DTA, downward is a direction of an endothermic reaction), and (b) quadrupole mass spectroscopy (QMS) profiles during heating process of LiBH_4 . In the QMS profile, the other impurity gases, including B–H related gases, were not detected within the accuracies of the apparatus.

Therefore, the purpose of the present study is to experimentally clarify the formation condition and the local atomistic structure of the intermediate compound of LiBH_4 .

The powder of LiBH_4 (95% purity, Aldrich Co. Ltd.) was examined by thermogravimetry and differential thermal analysis (TG-DTA, Rigaku TG8120, He flow with 150 ml/min and heating with 5 K/min) and quadrupole mass spectroscopy (QMS, ANELVA M-200QA, directly connected with the TG-DTA apparatus). Also, a part of the powder of LiBH_4 was heated up to 473, 573, 673, and 743 K, with 1 min holding, under 1 MPa of hydrogen (99.999 99% purity). The samples before and after heating were, then, characterized by powder x-ray diffraction measurement (XRD, Panalytical X'pert with $\text{Cu } K\alpha$ radiation), and laser Raman spectroscopy (RS, Nicolet, Almega-HD, 532 nm laser). The methods for handling complex hydrides with avoiding (hydro-)oxidation have been described elsewhere.^{22,23}

TG-DTA and QMS profiles of LiBH_4 are summarized in Fig. 2. As indicated in Fig. 2(a), there are two endothermic peaks at approximately 380 and 550 K corresponding to the structural transition and melting reaction of LiBH_4 , respectively.^{3,6,24} There is no dehydriding reaction in the former, but a very small amount (<0.2 mass %) of hydrogen is detected in the latter by the TG [Fig. 2(a)] and QMS [Fig. 2(b)] profiles. Upon heating, the superimposition of two more endothermic features is observed at approximately 700 and 800 K. The drastic weight losses, approximately 11 and 3 mass %, begin to appear at 700 and 730 K in the TG profile, and the amounts are consistent with the two-step dehydriding reactions expected from Eq. (2). The corresponding superimposition of the sharp and broad dehydriding peaks is observed in the QMS profile at the similar temperature range, at approximately 700 and 800 K. These results indicate that LiBH_4 changes into the intermediate compound at 700–730 K.²⁵

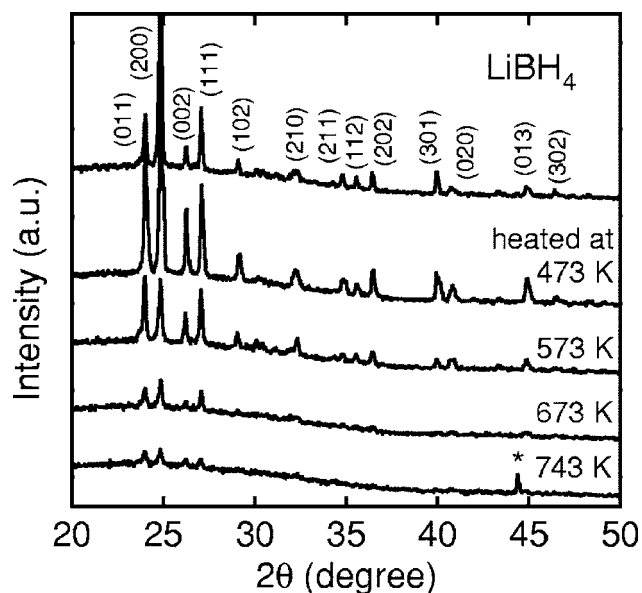


FIG. 3. Powder x-ray diffraction (XRD) profiles of LiBH_4 and its heated samples (measured at room temperature). The asterisk corresponds to the diffraction peak from the partially precipitated LiH , according to Eq. (1) and/or (2).

XRD has been employed to characterize the atomistic structures of the intermediate compound, and the results are shown in Fig. 3. With increasing heating temperatures, the intensities of the diffraction peaks become smaller without changing their peak positions. The diffraction peaks corresponding to the partially precipitated LiH can be seen in the sample heated up to 743 K, and only the diffraction peaks of LiH are observed in the sample heated up to 873 K. However, there is no diffraction peak of the intermediate compound despite strong intensities of the simulated diffraction peaks (not shown) from the atomistic structure model shown in Fig. 1, probably indicating that the compound does not possess long-range ordering in the structure.

Precise information about local atomistic structures on the B–H bonding can be obtained by RS measurements.^{24,26} So far, theoretically calculated Γ -phonon mode frequencies of some Li–B–H based phases have been reported,^{5,21} and the phonon density of states (PDOS) for the monoclinic $\text{Li}_2\text{B}_{12}\text{H}_{12}$ is indicated in Fig. 4(a). Also, actual Raman spectra of the same samples examined by the XRD are shown in Fig. 4(b). In the samples heated up to 673 K, both the B–H bending and stretching modes around 1300 and 2300 cm^{-1} , respectively, are not affected and stay similar frequencies to those of LiBH_4 without heating. However, it should be emphasized that the additional B–H bending and stretching modes around 600–1000 cm^{-1} and 2500 cm^{-1} , respectively, appear in the sample heated up to 743 K. They are coming from neither LiH nor (hydro-)oxides, but fairly consistent with the PDOS theoretically calculated for the monoclinic $\text{Li}_2\text{B}_{12}\text{H}_{12}$. Therefore, a possible intermediate compound of LiBH_4 is estimated, experimentally as well as theoretically, to be the monoclinic $\text{Li}_2\text{B}_{12}\text{H}_{12}$.²⁷

In summary, LiBH_4 starts to change into an intermediate compound at the temperature range over 700 K, accompanying the partial dehydriding reaction. Although the compound does not show long-range ordering for the powder x-ray diffraction measurement, the local atomistic structure can be investigated by the laser Raman spectroscopy; the B–H

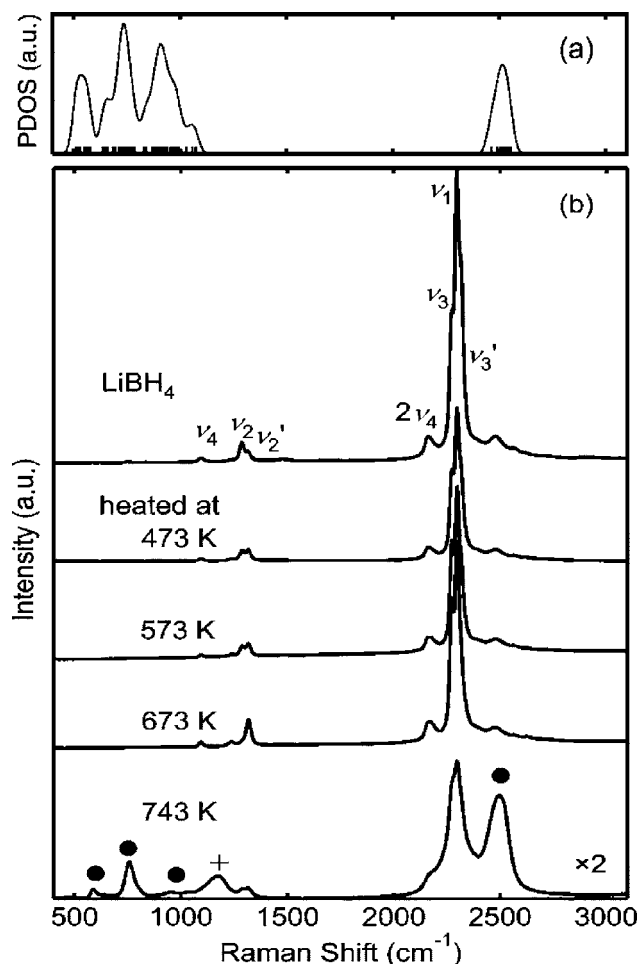


FIG. 4. (a) Calculated Γ -phonon mode frequencies of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and (b) laser Raman spectra of LiBH_4 and its heated samples (measured at room temperature). The close circles and plus correspond to the Raman modes due to the B–H bonding in $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and the B–B bonding in the partially precipitated α -B phase according to Eq. (1) and/or (2), respectively.

bending modes have lower frequencies as compared to those of LiBH_4 , while the B–H stretching modes appear at higher frequencies. These features are fairly consistent with the theoretical calculation on the monoclinic $\text{Li}_2\text{B}_{12}\text{H}_{12}$, consisting of Li^+ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ ions, as a possible intermediate compound of LiBH_4 . The further experimental studies on the atomistic and electronic structures of the compound, and also on the dehydriding and rehydriding reactions of LiBH_4 using appropriate intermediate compounds are now in progress.

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