High-pressure x-ray diffraction study on lithium borohydride using a synchrotron radiation

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Abstract. Lithium borohydride (LiBH₄) was compressed up to 10 GPa using a diamond-anvil-cell to investigate its high-pressure structure. In-situ x-ray diffraction profiles indicated a pressure-induced transformation at 1.1 GPa, which was consistent with the previous experimental observation such as Raman scattering spectroscopy. The high-pressure phase was indexed on a tetragonal symmetry of $P4_2/mmc$, which was not corresponding some structural models proposed by previous calculation studies. An unknown substance (presumably another Li-B-H compound), which was contained in the starting material, also transformed into its high-pressure phase at 0.6 GPa without any relation to the transformation of LiBH₄.

1. Introduction

Ternary light-element hydrides of alkali borohydrides are attractive as novel hydrogen-storage materials due to their gravimetric densities of hydrogen. Especially lithium borohydride, LiBH₄, has extremely high hydrogen content of 18 mass %.

Recently a densification of LiBH₄ has been simulated in some theoretical-calculation studies [1-3]. Also, very recently, Talyzin et al. [4] have reported that a high-pressure transformation of LiBH₄ was observed between 0.8 and 1.1 GPa using Raman scattering and x-ray diffraction measurement. However, the structure of high-pressure phase has not clarified in the experimental result yet.

In this study, we have examined in-situ high-pressure x-ray measurement using a synchrotron radiation to investigate the high-pressure structure of LiBH₄.

2. Experimental section

The samples (purity > 95%) were purchased from some chemical makers [5]. They were crushed with an agate mortar and loaded into a diamond-anvil-cell (DAC) in an argon atmosphere. The DAC consists of a pair of diamond anvils of 1/4 carat with a culet of 800 µm in diameter and a gasket (Inconel 700, 250 µm in thickness) with a hole of 400 µm in diameter. Some ruby balls were loaded with the sample into the gasket hole (a sample chamber) as a pressure marker. No pressure medium was used because any contamination should be avoided.
Angle-dispersive x-ray diffraction (XRD) using synchrotron radiation was performed at a bending magnet beamline BL-18C of Photon Factory (PF) in High Energy Accelerator Research Organization (KEK). The x-ray beam was monochromatized to energy of 20 keV and introduced to the specimen in the DAC through a pinhole collimator with 60-100 µm in diameter. Each diffraction pattern was obtained by exposing an image-plate detector for 30-60 min. In-situ XRD measurement was performed up to the pressure of 10 GPa at room temperature.

The diffraction peaks in the x-ray profiles were individually analyzed by fitting of the peaks with Pearson VII function. The structure was determined from the consideration of site symmetries of the space groups and systematic absences of the diffraction peaks. Lattice parameters were refined with the peak positions using the least-squares procedure of the Appleman-Evans program [6].

3. Results and discussion

3.1. Starting material

The starting materials loaded into DAC were identified using XRD before compression. A XRD pattern of the starting material and its integrated profile are shown in figure 1 (a) and (b), respectively.

The diffraction rings shown with arrows in figure 1 (a) correspond to peaks with open circles in figure 1 (b), which were identified as a room-temperature (ambient-pressure) phase of LiBH₄ [7]. Besides the peaks of LiBH₄ many other peaks are also observed in the diffraction profile. In the previous publications, two kinds of phase for LiBH₄, room-temperature phase and high-temperature one at ambient pressure, have been reported [8]. However, the peaks do not correspond to the high-temperature phase of LiBH₄. Also, they could not be identified as any oxides/hydroxides of lithium and/or boron, which are included in ICDD (International Center for Diffraction Data). The unknown substance shows the diffraction rings with some strong spots as shown in figure 1 (a). It suggests that the unknown substance is crystalline and fine, and denies the assumption that it has been formed in the reaction of LiBH₄ with the atmospheric moisture. The same unknown peaks have been observed also in a previous report [9] but they have never been identified.

Namely, the starting material consists of the room-temperature phase of LiBH₄ and other unknown substance. All of the "LiBH₄" powders purchased from the chemical makers contained the same substance. The fact should be noted especially in experiments of spectroscopic works. In the present study, we carefully observed the influence of the substance in the high-pressure behavior of LiBH₄.

![Figure 1](image_url)

**Figure 1.** (a) XRD pattern of the starting material in DAC before compression and (b) its integrated profile. The background due to x-ray scattering from air and diamond windows is not subtracted. The diffraction rings emphasized with arrows in (a) and the peaks with open circles in (b) correspond to the ambient phase of LiBH₄.
3.2. Observation of high-pressure structural changes

In-situ high-pressure XRD patterns up to 2GPa are shown in figure 2. At 0.6 GPa, all of the unknown peaks disappeared at the same time and new peaks appeared, which means the unknown peaks should be assigned to a single substance and it was transformed into its high-pressure phase at the pressure. The substance might be another Li-B-H compound.

LiBH₄ was transformed to a high-pressure phase at about 1.1 GPa without any relation to the unknown substance. It is consistent to the previous report, in which a pressure-induced transformation has been observed using Raman scattering spectroscopy by Talyzin et al [4]. Additional transformation did not occur in the compression up to 10 GPa. In decreasing the pressure, the high-pressure phase was reversed into the ambient-pressure form of LiBH₄ at 0.5 GPa.

![Figure 2](image-url)

**Figure 2.** High-pressure XRD patterns of LiBH₄ pressurized up to 2GPa.

3.3. Structure of the high-pressure phase of LiBH₄

The structure of the high-pressure phase was analyzed with the XRD profiles. The previous calculation studies have proposed some space groups: monoclinic structure Cc [1], P2₁/c [2] and tetragonal structure P4_{2}2_{1}c [3]. However, they could not explain the present diffraction profiles.

In our analysis of the XRD profiles obtained, the high-pressure structure was successfully indexed on a tetragonal symmetry with the dimensions of a = 3.801(1) Å, c = 6.509(4) Å at 1.1 GPa. The diffraction peaks at the condition and the indices are listed in Table 1. The systematic absences of the diffraction peaks suggested the space groups P4_{2}2_{1}c (No. 112). Previous Raman scattering results [4] has suggested that a tetrahedral molecular anion of [BH₄]⁻ in LiBH₄ remains even in the high-pressure structure after the transformation. However, the coordination of the space group P4_{2}2_{1}c does not allow the tetrahedral molecule in the structure. From the consideration of site symmetries of the space groups and the existence of the tetrahedral anion, the crystal structure of high-pressure phase should be proposed as the space group P4_{2}2_{1}c.

Figure 3 shows a schematic drawing of the structure estimated. Positions of hydrogen atoms were presumed to be located between lithium and boron because the B-H length (1.04-1.25 Å at ambient
pressure) is enough shorter than the Li-B distance in the high-pressure phase (2.50 Å at 1.1 GPa). In the future work, a high-pressure neutron diffraction measurement and a detailed analysis using Rietveld refinement should be performed in order to determine the atomic positions of hydrogen.

| Peak No. | d obs. (Å) | d calc. (Å) \(^a\) | hkl   |
|---------|-----------|----------------|-------|
| 1       | 3.803     | 3.801          | 100   |
| 2       | 3.284     | 3.282          | 101   |
| 3       | 2.687     | 2.688          | 110   |
| 4       | 2.472     | 2.472          | 102   |
| 5       | 2.073     | 2.072          | 112   |

\(^a\) These d-values were calculated on a tetragonal symmetry with the dimensions of a = 3.801(1) Å, c = 6.509(4) Å.

**Figure 3.** The structure of ambient-pressure phase of LiBH\(_4\), orthorhombic \(Pnma\) \(Z=4\), (left) and that of high-pressure phase proposed in the present study, tetragonal \(P4_2/mmc\) \(Z=2\), (right).

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