

High-pressure structural changes in a low-Z hydride LiBH_4

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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, LiBH_4 , has extremely high hydrogen content of 18 mass %.

It is indispensable to explore a denser form of the light element hydride in order to design a novel and higher density hydride. Recently a densification of LiBH_4 has been simulated in some theoretical-calculation studies [1-3]. Talyzin et al. [4] have reported that a high-pressure (HP) transformation of LiBH_4 was observed between 0.8 and 1.1 GPa using Raman scattering and x-ray diffraction measurement. However, the structure of HP phase has not clarified in the experimental result yet.

In this study [5], we have examined *in-situ* HP x-ray measurement using a synchrotron radiation to investigate the high-pressure structure of LiBH_4 .

Experimental section

LiBH_4 powder (Alfa-Aesar, purity > 98%) was loaded into a diamond-anvil-cell (DAC) in an argon atmosphere. Angle-dispersive x-ray diffraction (XRD) was performed at a bending magnet beamline BL-18C. 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 31 GPa at room temperature.

Results and discussion

LiBH_4 was transformed to a high-pressure phase (HP-1) at about 1.1 GPa. It is consistent to the previous report using Raman scattering spectroscopy [4]. The systematic absences of the x-ray diffraction peaks suggested the space groups $P4_2/mmc$ (No. 131).

The high-pressure form HP-1 was transformed to another high-pressure phase (HP-2) at about 16 GPa. The structure of HP-2 was indexed on a tetragonal symmetry. The two peaks of 110 and 002 in the tetragonal cell are approached with each other with increasing pressure and are finally superposed as a single peak at about 31 GPa, where the structure was indexed on a cubic symmetry, space group $Fm-3m$ (HP-3).

Upon reconsidering the matter, the HP-2 phase should have the subgroup symmetry of $Fm-3m$. The systematic absences suggested the possibility of the space groups $I4/mmm$, $I-42m$ or $I-4m2$ for HP-2 phase. However, the site symmetry of $I4/mmm$ does not allow an atomic distribution of the $[\text{BH}_4]$ tetrahedral molecule in the structure. Therefore, we concluded $I-42m$ or $I-4m2$ as a space group of HP-2 phase.

References

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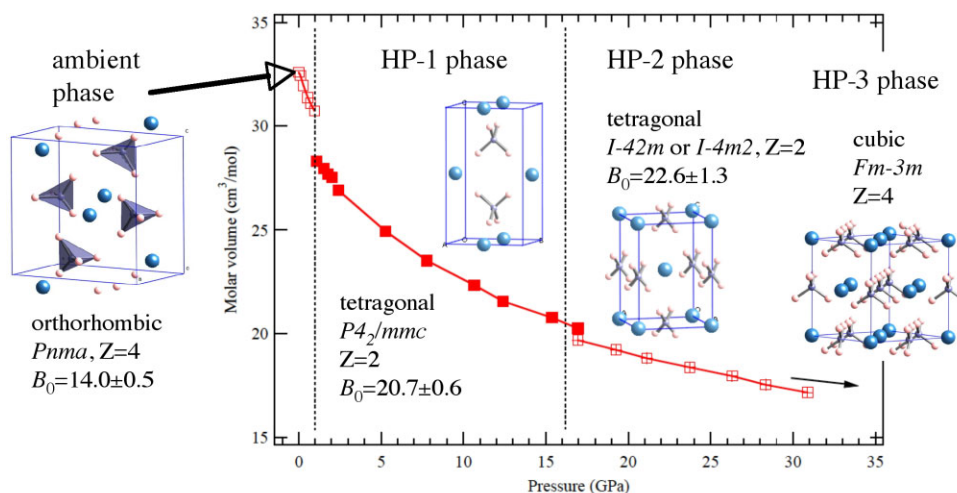


Figure 1. Structures of high-pressure phases of LiBH_4 and their molar volumes.