

Volume change of LiBH₄ under high temperature and high pressure

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Introduction

Lithium ion conductors are expected to become a solid electrolyte for use in Li-ion batteries. Recently, it was reported that a lithium borohydride (LiBH₄) exhibits high ion conductivity at high temperature phase (phase I) [1]. Such complex hydrides attract attention as a new type of lithium ion conductor. We set a goal to clarify the relation between the Li-ion conductivity and the structural change for several phases of lithium based complex hydrides. Existence of phase III and V of LiBH₄ under high pressure have been reported [2]. However, a high-pressure high-temperature phase diagram of LiBH₄ remains undetermined. Recently, we proposed a new structural model for phase III as *I4/acd* structure, and found a new metastable high-pressure phase V' [3].

In this study, we performed powder X-ray measurements under high temperature and high pressure for phase V of LiBH₄ in order to clarify the structural change. Phase V shows higher ionic conductivity than phase III, while the conductivity is lower than superionic phase I [4]. In addition, we report results of Raman and a.c. impedance measurements, which were performed in order to determine the pressure–temperature phase diagram of LiBH₄, and to obtain the change in ionic conductivity under high pressure.

Experimental

LiBH₄ was purchased from Alfa Aesar (purity > 95%). High-pressure was generated using a diamond anvil cell (DAC) with a diameter of 48 mm and a height of 30 mm. The anvil of the x-ray exit side was mounted on a B₄C backing-plate. The LiBH₄ crystal was loaded into the sample chamber of DAC with ruby ball in a high-purity argon atmosphere. The DAC was heated with a cartridge heater. The in-situ x-ray diffraction measurements under high-temperature and high-pressure were performed using synchrotron radiation at PF-BL18C at High Energy Accelerator Research Organization (KEK). Diffracted x-rays were detected by an imaging plate.

Results and discussion

Pressure–temperature phase diagram of LiBH₄, and a I–V phase boundary was determined experimentally with Raman measurement. The I–V phase boundary has a negative slope as same as a III–V phase boundary. This is consistent with the phase V to be a disorder phase. We succeeded in measuring the relative change in the ionic conductivity of LiBH₄ at pressures up to 3 GPa at 400 K with the a.c. impedance measurement. Ionic conductivity

for phases I and III decreased with pressure. Activation volumes at 400 K were estimated to be 5.0 cm³/mol for phase I and 6.4 cm³/mol for phase III on compression processes.

Powder x-ray patterns for phase V were obtained at 510 K in the range from 4 to 28 GPa. The molar volume versus pressure are plotted in Fig.1. The molar volume of phase V are smaller than that of phase III. This result is consistent with the III–V phase boundary to be negative. On the other hand, the molar volume of phase V is larger than that of phase V'. This would be explained by thermal expansion, because the measured temperatures are different.

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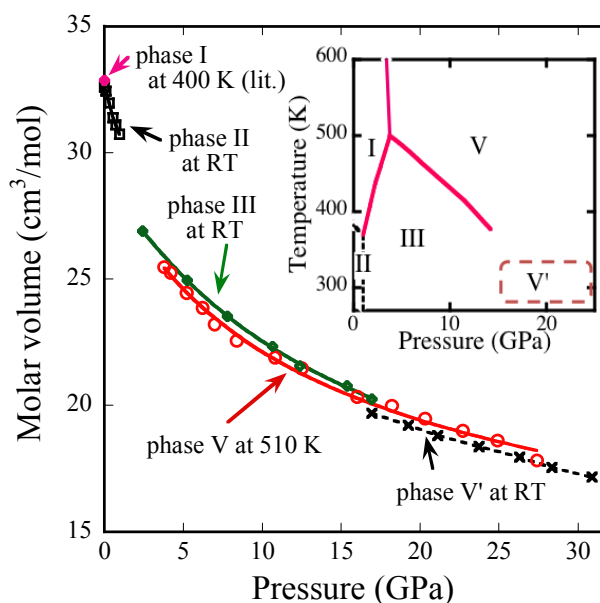


Figure 1: Molar volume of some phases of LiBH₄ against pressure. The inset shows a high-pressure high-temperature phase diagram of LiBH₄.

References

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