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High-pressure phase transition in $LiBH_4$

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Abstract

The high-pressure phase transition from ambient pressure α-$LiBH_4$ to high-pressure β-$LiBH_4$ was observed by Raman spectroscopy and X-ray diffraction between 0.8 and 1.1 GPa. The phase boundary between these two phases was mapped over a large range of temperatures using thermal conductivity studies and differential thermal analysis. The structure of the high-pressure phase could not be identified due to small number of experimentally observed reflections, but it was shown that it is different from previously reported theoretical predictions.

Keywords: High pressure; Borohydrides; Phase transition; Raman spectroscopy

1. Introduction

Complex hydrides (alanates and borohydrides) have attracted considerable attention recently due to their possible application as hydrogen storage materials. High-pressure studies for some of these materials were performed already about half-century ago but in spite of this only limited information is yet available. Much of the recent activities in high-pressure studies of these materials was stimulated by theoretical studies performed by Vajeeston et al. who predicted a large volume collapse for high-pressure modifications of $LiAlH_4$ and $NaAlH_4$ [1,2]. Experimental studies showed that phase transitions do occur in these materials at high-pressure conditions, though not exactly into the predicted structures [3,4]. Similar studies have recently been initiated also on borohydrides. Two high-pressure phase transitions were observed experimentally for $NaBH_4$ using diamond anvil cell (DAC) methods and thermal conductivity measurements [5–7].

The ambient phase of $LiBH_4$ was recently studied in detail due to the interest in the hydrogen storage properties of this material. Both the Raman spectrum and the crystal structure of this phase are well known. At room temperature and normal pressure $LiBH_4$ crystallizes in an orthorhombic structure (space group *Pnma*, $a = 7.17858(4)$, $b = 4.43686(2)$, $c = 6.80321(4)$) Å [8]. It is usually described to be composed of tetrahedral $(BH4)^-$ anions and Li^+ cations. A structural transition was reported to occur in this phase upon heating, at ~381 K [9–11]. According to more recent data this phase transition involves also some minor loss of hydrogen and the exact nature of this transition is not clear at the moment [12]. Borohydrides with *fcc* lattice-related structure ($NaBH_4$, KBH_4, $RbBH_4$, $CsBH_4$) are known to undergo phase transitions into more ordered phases at low temperatures and ambient pressure [13,14]. However, the crystal structure of $LiBH_4$ is different from that of the above compounds and no phase transition has been observed at low temperatures at atmospheric pressure [15]. On the other hand, a very careful study of phase transformations in $LiBH_4$ at high pressure, at and above room temperature, was carried out by Pistorius [11] about 40 years ago. Until now, this remains the only available experimental study in this field. A phase transition into an almost 6% denser high-pressure phase was observed in Pistorius' volume measurements to occur at around 0.6 GPa at 298 K and 0.84 GPa at 341 K [11], but the transition was associated with a quite large hysteresis. This new phase was stable to the highest pressure investigated, 4.5 GPa. Two additional high-pressure phases

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were observed above 370 K, but since structural data were not collected in this study the natures of these three high-pressure phases are unknown. Recently, the structural stability of $LiBH_4$ was studied theoretically by several groups. Łodziana et al. [16] predicted a phase transition into a monoclinic high-pressure phase with space group Cc to occur at ~3 GPa. Another theoretical prediction was recently given by Vajeeston et al. [17]. In this study, a phase transition into the tetragonal β-KBH_4 type of structure was proposed to occur at 6.2 GPa. The high-temperature hexagonal phase of $LiBH_4$ was predicted to be stable at pressures below 6.2 GPa and assumed to be the high-pressure phase found by Pistorius [11]. A third study by Frankcombe et al. [18] suggests that $LiBH_4$ should transform first into a $P2_1/c$ phase at 1 GPa, then into the Cc structure near 2.2 GPa.

We present the results of a set of experiments performed using the DAC. Raman spectra and XRD patterns were collected at pressures up to ~9 GPa at room temperature. We have also used thermal conductivity measurements and differential thermal analysis (DTA) as a tool to map for the first time the phase transition boundary between the ambient pressure α-$LiBH_4$ and high-pressure β-$LiBH_4$ phases to below 200 K. We show that this transition has a very large hysteresis and present the high-pressure phase diagram of $LiBH_4$ below 370 K.

2. Experimental details

$LiBH_4$ of 99.9% purity was purchased from Sigma–Aldrich and used without additional purification. Raman spectra and XRD data recorded on the purchased powder showed only $LiBH_4$ without any peaks from impurity phases. High-pressure experiments were performed using a DAC with 0.4 mm flat culets. The sample was loaded into a 0.2 mm hole in the steel gasket together with a ruby chip used for pressure calibration. In the XRD experiments, a small piece of gold wire was added for calibration. No pressure medium was used. The initial thickness of the sample was 60–70 μm. Since the material is sensitive to moisture, the loading was performed in a glovebox under argon gas. Raman spectra of the starting material and for the sample loaded into the DAC were identical, which confirmed that the loading procedure had not affected the sample. The pressure was increased gradually in steps of 1–1.5 GPa, and Raman spectra were recorded at every step during compression and decompression. Usually, the time of treatment at each pressure step was about 1–2 h. A Renishaw 1000 Raman spectrometer with a 633 nm excitation laser and a resolution of $2\,cm^{-1}$ was used in these experiments. Raman spectra were recorded in situ through the diamond anvils using long focus ×20–50 objectives.

The XRD data were recorded with a system consisting of Rigaku FRD high-brilliance generator (90 kW) and an APEX CCD Area Detector. The Mo$K\alpha$ radiation (tube voltage 60 kV, tube current 55 mA, cathode gun $0.1 \times 0.1\,mm^2$) was focused with MaxFlux X-ray optics and further collimated down to 40 μm FWHM beam size. The two-dimensional XRD patterns were integrated using Fit2D software.

As in a previous experiment [7], the thermal conductivity κ was measured using the hot wire method [19] with a 0.1 mm in diameter Ni wire probe. In the present experiment, half of the cylindrical pressure cell was filled with solid Teflon® and the remaining semi-circular segment filled with $LiBH_4$ powder, packed as dense as possible. The Ni wire probe was arranged inside the specimen at a constant distance from the periphery to minimize pressure gradients, since there is always a small radial flow of material on compression. The pressure in the cell was determined from load/area with an empirical correction for friction, established in a separate experiment using the pressure dependence of the resistance of a Manganin wire. To enable detection of phase transitions also by DTA, one type K thermocouple was placed in the sample and another one in the bottom of the Teflon® capsule. The sign and magnitude of the output voltage difference between these two thermocouples was monitored continuously. The pressure cell was filled in a glove-box under dry argon gas. The thermal conductivity and DTA experiments were carried out in an all-steel piston-and-cylinder device, 45 mm in inside diameter. The cylinder was fitted with an electrical heater and insulated by fibreglass insulation, and could be cooled by direct spraying with liquid nitrogen. A simple on/off regulator could keep the pressure cylinder at a reasonably constant temperature both above and below room temperature. The large thermal mass of the cylinder ensured good short-time temperature stability.

3. Results and discussion

3.1. Raman study in DAC

The Raman spectrum of $LiBH_4$ at ambient conditions is well known [20,21]. The high-frequency region exhibits several peaks due to internal $B-H$ vibrations and some combinational modes. In our spectra, the major peaks are found at 2320, 2300, 2275, 2181, and 2161. The intermediate-frequency region shows four peaks due to bending modes in the range from 1000 to $1400\,cm^{-1}$. Finally, the low-frequency region below $600\,cm^{-1}$ exhibits librational and translational modes. These peaks were too weak to be observed in our high-pressure experiments. The spectrum recorded from the pristine material was in good agreement with literature data [20].

Raman spectra of $LiBH_4$ recorded while increasing the pressure are shown in Fig. 1. Comparing spectra recorded at 0.5–1.4 GPa, clear changes are visible. These changes are interpreted in terms of a phase transition from ambient pressure α-$LiBH_4$ to a high-pressure β-$LiBH_4$ phase, in good agreement with the previous study by Pistorius [11] who observed a transition at ~0.7 GPa at room