Synchrotron Radiation X-Ray Diffraction Studies of $LiBeH_3$

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Introduction

The search for light metal hydrides as a potential high-T_c conventional, electron-phonon mediated, superconductors began following Overhauser's [1] suggestion that a new class of light metal hydrides with a modified perovskite structure could exhibit unusual properties. He argued that the electron density in these compounds could be high and this coupled with the large amplitude of the hydrogen vibration could make this class of light metal hydrides an ideal candidate for high-T_c superconductors. Among metal hydrides the $LiBeH_3$ and Li_2BeH_4 compounds have been proposed as candidates for high-T_c superconductivity since the positions of hydrogen atoms in the respective crystal structures were suggested to lead to the formation of hydrogen atom-based conduction bands. Moreover, electronic properties of these metal hydrides are expected to be particularly influenced by the light mass of hydrogen. What is more, the large vibrational amplitude of hydrogen could give rise to strong electron-phonon coupling effects, especially if the hydride remains metallic with a high electronic density of states at the Fermi energy.

Since Overhauser's work, a number of theoretical studies of the electron band structure and density of states using a variety of methods and models have been carried out. However the results of these studies, including electronic band-structure, total energy, bulk modulus, density of states, and charge distribution calculations reported are controversial [2-4]. Some of these estimations eliminate the possibility of Li-Be hydrides being metallic indicating a large band gap for these compounds, yet some have found them to be isolators and others to be semiconductors. Although it is generally assumed that Li-Be hydrides are not metallic and do not have such a high electron densities as suggested by Overhauser [1] some of a recent band–structure calculations indicated its strong resemblance to high-temperature superconductors but only when vacancies were introduced into the hydride structure. Many authors conclude that better samples are needed to reach a definite conclusion. Therefore, the question of superconductivity in these compounds remains open.

The motivation for our work was the fact that some of the theoretical studies have predicted the possibility of structural transitions of Li-Be hydrides to metallic phases [5, 6]. In particular there have been suggestions regarding the possibility of pressure-induced metallization of the supposed insulating structures. More broadly, polymorphism of Li-Be hydrides has been predicted theoretically. For example, it has been postulated that only a small reduction in the lattice spacing of $LiBeH_3$ (from 2.545 to 2.459 Å) would be required to change the material from isolating/semiconducting to metallic [7]. Moreover the possibility of superconductivity was suggested at still higher electronic densities, which could be produced under applied pressure, by impurity doping Li-Be hydrides, as well as by the introduction of hydrogen vacancies.

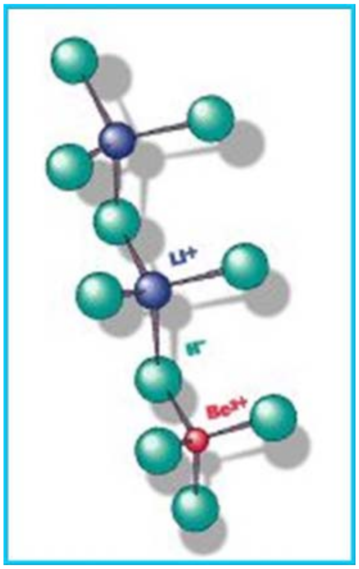

Fig. 1 $LiBeH_3$ associates atoms of hydrogen (green), beryllium (red), and lithium (blue), that are three of the four lightest elements of the universe. Theoretical works predict that the assembly of such small atoms could make a very dense structure and display extraordinary physical properties.

The goal of our project is to investigate the effect of pressure compression on the modification of crystal structure of Li-Be hydrides and follow the possible pressure-induced phase transitions. In the first step of the project we synthesized $LiBeH_3$ (Fig. 1) using an organo- metallic synthetic procedure [8] and we used synchrotron-radiation x-ray diffraction technique to determine its crystal structure.

Methods and Materials

$LiBeH_3$ hydride in addition of being toxic can react violently in contact with oxygen. Therefore all sample handling had to be carefully performed in an inert atmosphere-filled glove box. For synchrotron x-ray diffraction studies a few grains of the synthesized hydride were inserted into a quartz capillary that was immediately sealed with an epoxy resin which is impermeable to air. All x-ray diffraction patterns were collected at the 16-ID-B undulator beamline at the High Pressure Collaborative Access Team (HPCAT), sector 16 of the Advanced Proton Source at Argonne National Laboratory, using a monochromatic beam of 0.4297 Å wavelength. The diffracted x-rays were collected with an image plate (Mar-345) detector placed 353 mm from the samples. The 100 µm x 100 µm x-ray beam was achieved by microfocusing with two Kirkpatrick-Baez mirrors and a 30 µm diameter Mo cleanup pinhole to eliminate the beam-tails. The diffraction pattern was analyzed by integrating of images as a function of 2 theta using the program FIT2D [9] to obtain a conventional, one dimensional diffraction profile. The diffraction pattern was processed with programs like Powder Cell 2.4 [10] Jade 6.5 [11], and General Structure Analysis System-GSAS [12, 13].

Results and Discussion

Several structures have been proposed for Li-Be hydrides, including a face-centered cubic (fcc) perovskite-type structure with a = 5.09 Å [1], monoclinic distorted perovskite-type structure with a = 4.42, b = 6.22, c = 4.64, β = 94.20° [14]. Other papers suggested for $LiBeH_3$ a hexagonal structure of ilmenite ($FeTiO_3$) with either a = 13.26 Å and c = 9.0 Å or a = 19.39 Å and c = 8.99 Å [15].

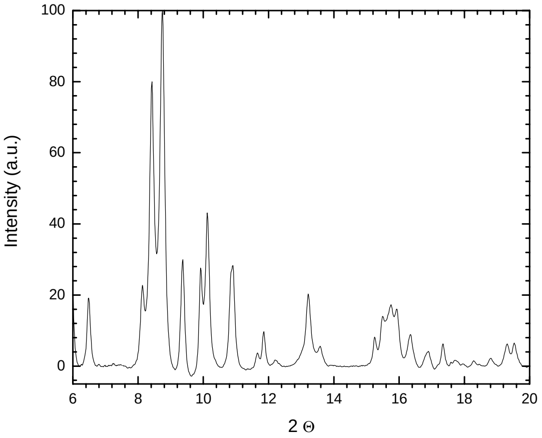

Fig. 2 Synchrotron x-ray diffraction pattern of $LiBeH_3$ collected at the 16-ID-B undulator beamline at the High Pressure Collaborative Access Team (HPCAT), sector 16 of the Advanced Proton Source at Argonne National Laboratory. The $LiBeH_3$ sample was enclosed in a sealed quartz capillary.

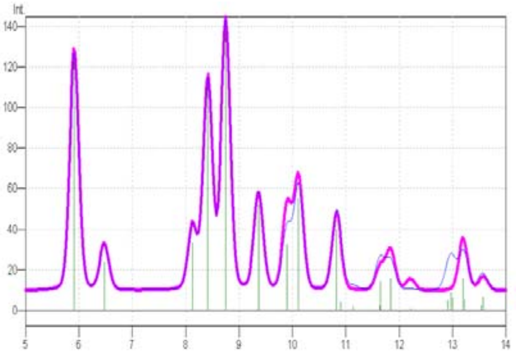

Fig. 3 Rietveld full profile refinement of the $LiBeH_3$ x-ray diffraction pattern collected at HPCAT. The crystallographic structure of our compound is different from that suggested in the literature. The refined unit cell is monoclinic.

Synchrotron x-ray diffraction pattern of the synthesized $LiBeH_3$, collected at HPCAT, is shown in Figure 2. The diffraction pattern suggests that the $LiBeH_3$ sample is composed of a single crystalline phase. The crystallographic structure of our compound is different from that suggested in the literature.

Figure 3 shows the Rietveld profile refinement [12, 13] of the diffraction pattern. The full-profile fit is excellent and explains all diffraction lines present. This powder pattern can be indexed using the monoclinic unit cell. The identified space group is C2/c (no. 15) and the refined unit cell constants are: *a* = 8.400 (0.008) Å, b = 4.976 (0.003) Å, *c* =6.224 (0.005) Å, β = 114.86° (0.07) with the cell volume V = 236.05 $Å^3$ [16]. The proposed crystallographic structure is closely related to Li_2CO_3 judging from the agreement of the unit cell parameters and volumes. Literature reports that for Li-Be hydrides chemical synthesis conditions often yield multiphase products instead of a single phase compound and that its structure can vary [17, 18]. We cannot also rule out the well known difficulties associated with the organometallic synthesis or the possible chemical transformation of the compound exposed to oxygen during manipulations. Therefore, in order to confirm the chemical composition of the synthesized compound a detailed chemical analysis is needed.

Acknowledgements

Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W 31 109 ENG 38. HPCAT is a collaboration among the Carnegie Institution, Lawrence Livermore National Laboratory, the University of Hawaii, the University of Nevada Las Vegas, and the Carnegie/DOE Alliance Center (CDAC).

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