

Interaction of Hydrogen on a Lanthanum hexaboride (111) Surface
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Abstract

In order to sustain society's current level of energy consumption and prevent irreversible climate degradation due to the greenhouse effect an alternative energy carrier is required.

The aim of this experiment was to determine the conditions under which a lanthanum hexaboride (LaB_6) surface would form boron-hydrogen (B-H) bonds when exposed to hydrogen. Reflection Absorption Infrared Spectroscopy (RAIRS) was used to confirm formation of bonds and X-ray Photoelectron Spectroscopy (XPS) and Low Energy Electron Diffraction (LEED) were used to characterize the surface. Upon completion of the experiment no B-H bonds were found to form under the conditions tested. However, it is believed that the bond formation may have been impeded by the tungsten contamination of the surface or that due to the instability of the B-H bond a lower temperature could be required for their formation.

Keywords

Lanthanum hexaboride, hydrogen, ultra high vacuum, boron hydrogen bonds, hydrogen atom source

Introduction

Currently, one of the most pressing challenges facing human society is the need to find alternative energy sources due to the dwindling fossil fuel supplies as well as the detrimental impact to the environment the burning of said fuels is having. An alternative to the current system is a hydrogen economy using hydrogen as an energy carrier. This approach is advocated by a 2003 report by Basic Energy Sciences encouraging research into the development of hydrogen usage, storage, and production technologies.¹ The most challenging of those three areas is finding a practical method of hydrogen storage. This experiment is designed to obtain further knowledge in the area of hydrogen storage by uncovering the fundamental properties of B-H bonds specifically in lanthanum hexaboride. By defining the conditions under which these bonds will form, a basic foundation of knowledge will be established upon which further research may be built. Boron hydrides hold significant potential as hydrogen storage materials due to their high weight percentage of hydrogen, the ability to store hydrogen reversibly, and for this reversibility to take place at relatively low temperatures and pressures due to the electron deficient nature of the bonds.²

LaB_6 in particular shows potential due to its ready adsorption and desorption of hydrogen in promoting a hydrogen-deuterium equilibrium. This is due to the lanthanum in the material acting as a catalyst for the reaction.³ It is also known that CaB_6 can be hydrogenated to $\text{Ca}(\text{BH}_4)_2$ and since CaB_6 and LaB_6 have the same structure it was believed that a similar hydrogenation of LaB_6 could occur. Furthermore, studies show that the LaB_6 (111) surface's top layer is composed of the triangular faces of the B_6 octahedra and that in forming this surface the interoctahedral bonds are broken resulting in three dangling boron bonds 55° from the normal and 120° apart (Fig. 1) allowing the hydrogen atoms easy access to reactive sites on the sample.⁴ Previous experiments conducted by the Trenary group exposing a LaB_6 (111) surface to molecular hydrogen have yielded no B-H bonds. Therefore, in the current experiment, atomic hydrogen was used in the belief that its more reactive nature would allow for B-H bond formation.

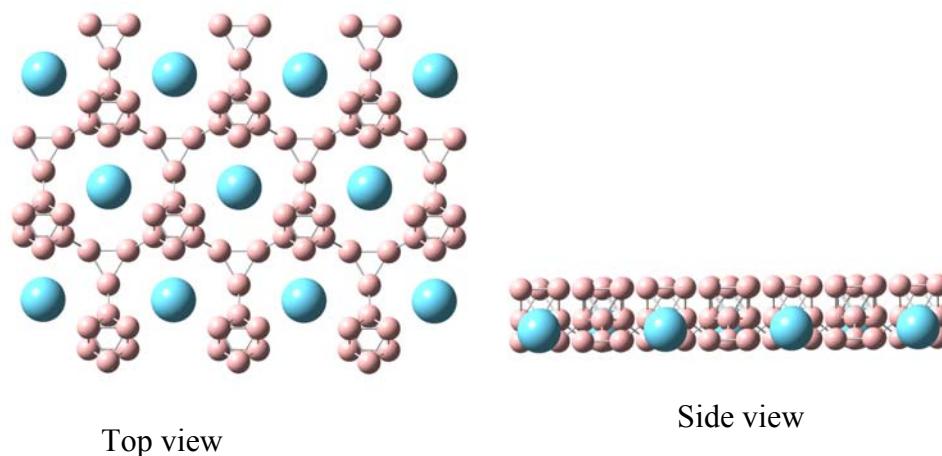


Figure 1: Top and side views of LaB_6 (111) surface.

Methods

The experiment required the construction of a hydrogen atom source. Of the many ways hydrogen atoms can be generated the most popular is passing hydrogen gas over a hot tungsten filament which thermally dissociates the H_2 molecules.⁵ The hydrogen atom source consists of a stainless steel doser over whose opening was mounted a .245 mm thick tungsten wire filament which is shielded by a ceramic cylinder. The filament was connected to a power source by ceramic insulated oxygen free copper leads and the ceramic shield held in place via tantalum foil spot welded to the doser (Fig. 2). The atom source was then installed into an ultra high vacuum (UHV) chamber ($\sim 4 \times 10^{-11}$ torr). The chamber was then baked out for 2 days to remove contaminants (mainly water), and all instrument filaments were degassed while the chamber was still warm. The UHV chamber has been described in detail elsewhere.⁶ In summary, it is equipped with low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and a Fourier transform infrared spectrometer (FTIR) for reflection absorption infrared spectroscopy (RAIRS). The infrared spectra were obtained using a Mattson model RS-10000 FTIR and the spectra were obtained at 4 cm^{-1} resolution and 1024 scans. The IR beam enters and exits the chamber through differentially pumped O-ring sealed KBr windows and an MCT (HgCdTe) detector with a SiC source and a scan range of 800 to 4000 cm^{-1} was used. The sample was aligned to provide the best IR signal and in cases where the sample was annealed to higher temperatures it was cooled back to room temperature before the spectrum was obtained. Backgrounds for those experiments were also taken at room temperature. In cases where the sample was cooled via liquid nitrogen both the background and the spectra were obtained at the cooled temperature. All RAIRS spectra were baseline corrected. The maximum temperature reached during annealing was 1363.15 K. Sample temperature was monitored with a C-type thermocouple attached to the upper tantalum foil piece which holds the sample in position. XPS was taken using a VG CLAM2 hemispherical analyzer and a dual anode X-ray source. Mg $K\alpha$ radiation

was used; the spectrometer was previously calibrated to have the Pt $4f_{7/2}$ peak at 71.2 eV. Pressure measurements are given based on readings from an uncorrected ion gauge. The hydrogen gas (99.9999%) was purchased from Matheson Tri-gas Inc. and used without further purification.

The sample is a single crystal of LaB_6 grown and cut at the National Institute for Materials Science in Tsukuba, Japan. The crystal was polished to a mirror finish before use and is a disk that has an approximately 1 cm diameter and is approximately 2 mm thick.

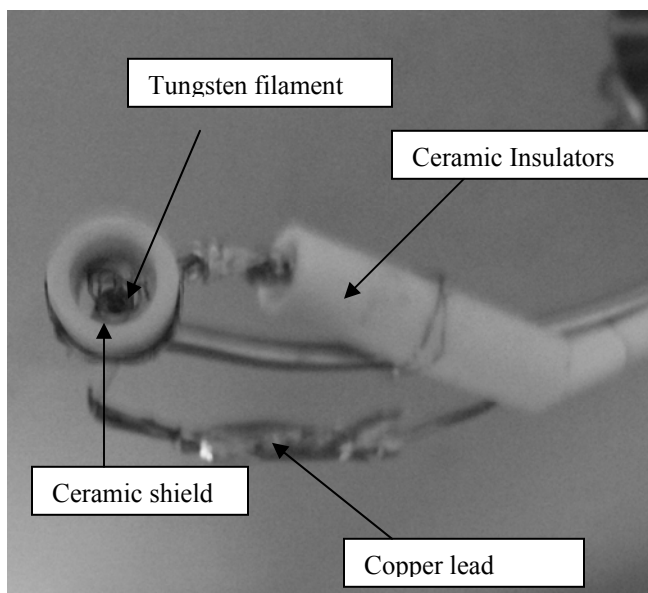


Figure 2: Hydrogen atom source.

Results and Analysis

The sample was exposed to a maximum of 1000 langmuir, ($1\text{L}=1\times 10^{-6}$ Torr s) of atomic hydrogen both at room temperature and at ~ 237.5 K. B-H stretches and bends were expected at 2500 and 1000-1200 cm^{-1} respectively, however, no evidence for the formation of B-H bonds was observed at any of the exposures.⁷ An IR spectrum of the sample at ~ 237.5 K and 1000 L exposure is presented below (Fig. 3). A single beam IR spectrum of the LaB_6 (111) surface is shown in figure 4. An XPS spectrum (Fig. 5) of the sample surface at room temperature was obtained to ensure no contaminants remained on the surface to impede a possible reaction. The surface appears to be relatively free of carbon and oxygen contaminants; however there are peaks corresponding to tungsten indicating some has been deposited on the surface from the filament. This may have impeded the ability of the sample to form B-H bonds. A sharp LEED pattern (fig. 6) for the sample was also obtained indicating a well-ordered surface with no restructuring.

This LEED pattern was taken prior to the XPS spectra and it is unknown if tungsten contamination was present at the time it was obtained. The lack of B-H bond formation may be due to the tungsten present on the surface which could have acted to block boron sites thus preventing the hydrogen from forming bonds with boron. It is also known that B-H bonds are unstable and it is possible that at the temperatures used they dissociated as

quickly as they formed thus lower temperatures would be required to allow more permanent formation.

LaB₆ (111)-1000 L atomic hydrogen, 237.5 K

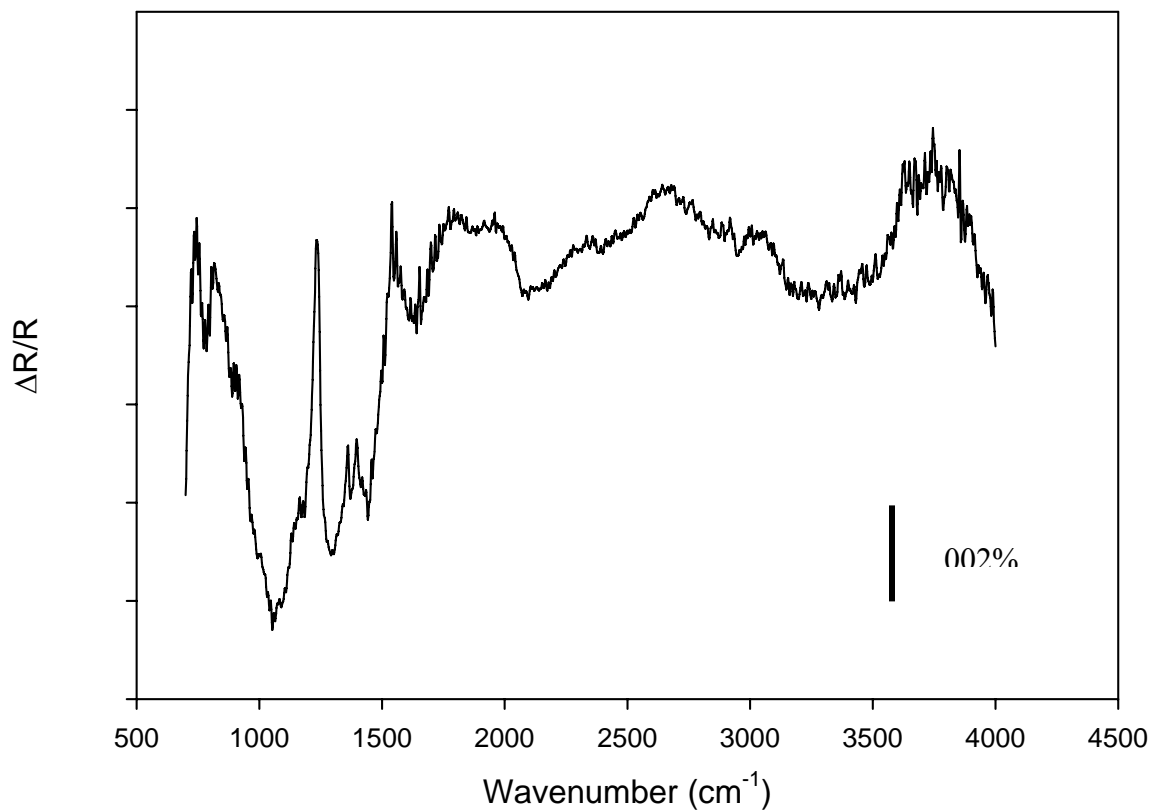


Figure 3: IR spectrum of LaB₆ after H-atom exposure of 1000 L atomic hydrogen at 237.5 K.

Lanthanum Hexaboride (111)

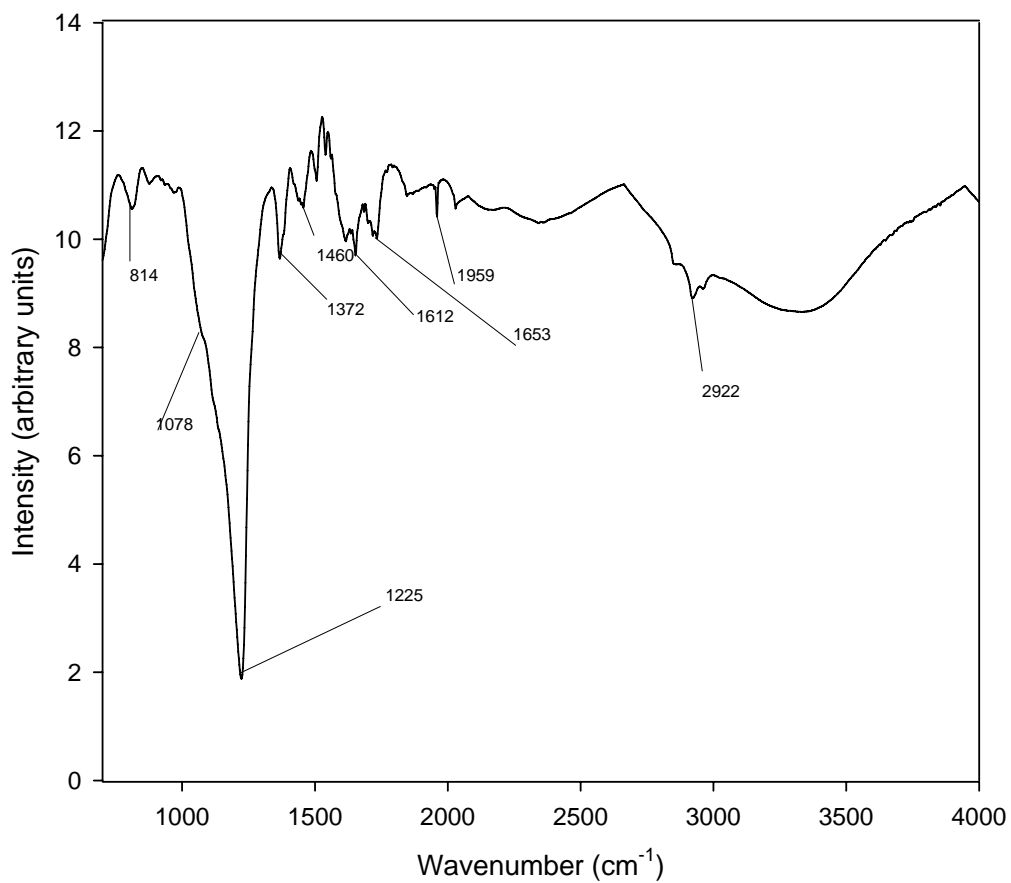


Figure 4: Single beam IR spectrum of LaB₆ surface.

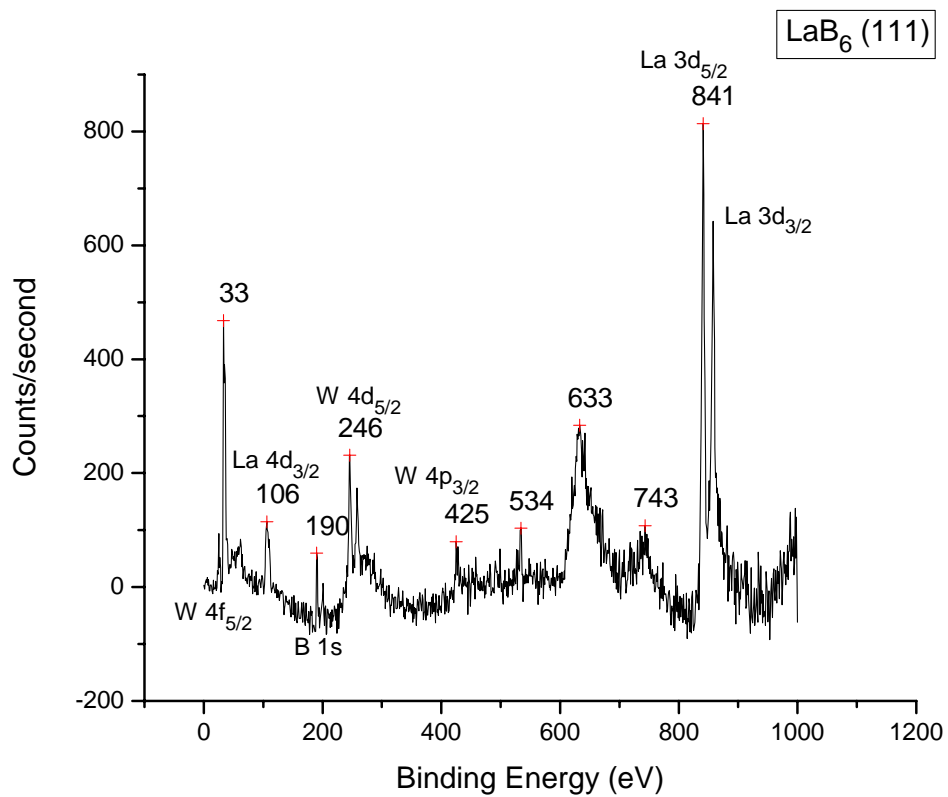


Figure 5: A XPS survey scan of the sample indicating tungsten contamination.

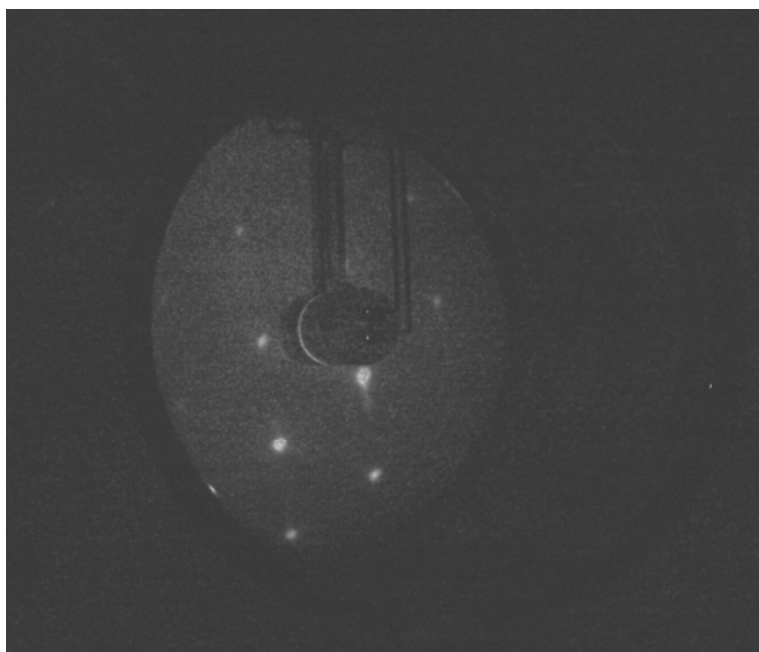


Figure 6: LEED pattern of LaB₆ after annealing to 1363.15 K.

Conclusion

Although no B-H bonds were found for this experiment, it is possible that bonds may occur at lower temperatures than those explored here. It is also possible that the tungsten deposited onto the sample from the filament prevented any reaction from occurring. It is therefore suggested that this experiment be tried again when tungsten is not present on the surface. Attempting experiments at lower temperatures may not be practical as special cooling to achieve these temperatures would be difficult to incorporate into an onboard hydrogen power supply, but nonetheless may also be a valid research avenue.

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