



# Chloride influence on the formation of lanthanum hexaboride: An in-situ diffraction study



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## ABSTRACT

LaB<sub>6</sub> has been a material of interest for decades due to its thermionic emission, plasmonic properties, and low work function, and researchers continue to discover new properties even now. In order to meet growing interest in customizing these properties, it is important to gain better control over the system and a better understanding of the fundamental mechanism of LaB<sub>6</sub> crystal growth and formation. Traditional synthetic methods require very high temperatures, at which point crystallization happens too quickly to be readily studied. Our discovery that LaB<sub>6</sub> may be made using lower temperatures has made it possible to slow down crystal formation enough for lattice growth to be observed. We report here an in situ diffraction study of the reaction between LaCl<sub>3</sub> and NaBH<sub>4</sub>. In observing the evolution of the (1 1 1), (1 1 0), and (2 0 0) lattice planes of LaB<sub>6</sub>, we have discovered that the Cl of LaCl<sub>3</sub> has a strong influence on crystal formation, and that excess Cl, temperature and heating rate may all be used as tools to control the LaB<sub>6</sub> final product.

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## 1. Introduction

Lanthanum hexaboride (LaB<sub>6</sub>) has become a material of intense interest in recent years due to its excellent thermionic emission properties and low work function [1,2], and with its strong NIR absorbance is gaining in popularity as a window coating to absorb solar heat [3,4,5]. Furthermore, the recent ability to make LaB<sub>6</sub> on the nanoscale is allowing new properties to be discovered [6,7]. In order to tune this material to meet desired applications, several synthetic routes have been explored, including chemical vapor deposition [8,9] arc plasma [2,10], and hydrothermal [11] processes. To better control the physical properties of LaB<sub>6</sub>, it is important to understand how the synthetic conditions influence crystal growth. The electronic and optical properties are strongly dependent upon the characteristics of the crystal lattice, and numerous publications report the ability to control morphology and particle size [9,11,12,13] as well as La vacancies [14]. Interestingly, every study to date on the growth of LaB<sub>6</sub> only observes the shape of particles after formation. Currently, there is no available research which provides insight into how the growth of the LaB<sub>6</sub> lattice evolves, and the inability to understand the reaction process limits researchers' ability to control the design of this material.

LaB<sub>6</sub> has been studied for decades and while some control has been achieved over particle size and shape, the mechanism behind lattice growth has gone unexplored. Perhaps the simplest and most traditional synthesis is the solid state reaction of lanthanum chloride (LaCl<sub>3</sub>) and sodium borohydride (NaBH<sub>4</sub>) at high temperatures ( $\geq 1200$  °C) [15,16]:  $\text{LaCl}_3 + 6\text{NaBH}_4 \rightarrow \text{LaB}_6 + 3\text{NaCl} + 12\text{H}_2 + 3\text{Na}$ . The byproducts are understood, but the driving force for this reaction and why is it possible to make LaB<sub>6</sub> on the nanoscale by simply reducing the reaction temperature remain mysterious [12,14a]. Furthermore, the heating rate also has a large influence on LaB<sub>6</sub> and may be used to control La vacancies in the system [14a]. However, it is unclear why the rate only exhibits this control between the melting point (400 °C) and decomposition (500 °C) of NaBH<sub>4</sub>. In order to answer these questions we collected in-situ diffraction measurements during the LaB<sub>6</sub> reaction at the Advanced Light Source (ALS), and have gained several insights into what influences crystal growth. By observing the evolution of the (1 1 0), (1 1 1), and (2 0 0) lattice planes, we have determined that the anion of the lanthanum precursor has a strong influence on crystal growth. Unexpectedly, we discovered that excess Cl in the reaction causes negative thermal expansion as LaB<sub>6</sub> grows. The small chlorine atoms act as bridging ligands between lanthanum atoms, and the anion, heating rate, and temperature are all important to controlling the formation of LaB<sub>6</sub>.

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## 2. Experimental methods

Anhydrous lanthanum (III) chloride (Strem Chemical), anhydrous lanthanum (III) iodide (Strem Chemical), sodium borohydride (EMD), sodium chloride (Sigma-Aldrich), and sodium iodide (VWR) were stored in an argon atmosphere glove box until used. All powders were well mixed and finely ground using a mortar and pestle in an argon atmosphere glove box and placed in 0.7 mm diameter quartz capillaries (Charles Supper Company) that were sealed with wax. Capillaries were mounted on a Huber sample stage on beamline 12.2.2 at the Advanced Light Source (ALS) at Lawrence Berkeley Laboratory. Diffraction data was collected on a Mar345 image plate/Perkin Elmer amorphous silicon detector using synchrotron radiation monochromated by silicon (1 1 1) to a wavelength of 0.4980 Å and a detector distance of 290 mm. Distance and wavelength calibrations were performed using a LaB<sub>6</sub> diffraction standard with the program Dioptas [17], which was also employed for radial integrations. Plotted data is estimated to be accurate within ±0.005°. All samples were radiatively heated using IR lamps on a SiC tube with a 2 mm outer diameter by 1 mm inner diameter. This miniature “tube furnace” was equipped with a thermocouple for accurate measurements of the sample temperature and was designed at the ALS [18].

## 3. Influence of Cl anions on LaB<sub>6</sub> growth (in-situ diffraction)

In the initial proof of concept reaction, a 1:6 M ratio mixture of LaCl<sub>3</sub> to NaBH<sub>4</sub> was heated in 100 °C increments using a 5 °C/s heating rate up to 600 °C. The sample was held at each temperature for two minutes and then diffraction was measured using a 30 s frame.

Additional in situ reactions used a 1:6 M ratio mixture of LaCl<sub>3</sub> to NaBH<sub>4</sub> (and a ratio of 1:6:0.2 for LaCl<sub>3</sub>/NaBH<sub>4</sub>/NaCl was used when “excess salt” was called). For 600 °C reactions the precursors were initially heated to 200 °C and held there for two minutes. The materials were then heated at a ramp rate of either 0.17 °C/s or 3 °C/s up to 600 °C and held at 600 °C for 30 min. Data collection started at 200 °C and was collected automatically every five minutes using a 40 s frame collection. For 400 °C reactions the precursors were initially heated to 150 °C and held there for two minutes. The materials were then heated at a rate of 0.17 °C/s to 400 °C and held at 400 °C for 30 min. Data collection started at 200 °C and was collected automatically every five minutes using a 40 s frame.

## 4. Results/discussion

We recently discovered that in the low temperature synthesis of LaB<sub>6</sub>, small Cl atoms from the lanthanum precursor stay within the crystal upon completion of the reaction, and thermogravimetric-mass spectroscopy (TGA-MS) analysis confirmed that Cl was removable upon heating [6]. From this study emerged a postulate that the anions must either exist freely within the crystal lattice or act as bridging-ligands between La atoms [6]. Unexpectedly, Raman data showed a change of only the stretching vibrational modes of the hexaboride cluster upon Cl removal, implying that Cl cannot reside between the octahedral boron cluster and La, so it must be bound somehow within the lattice. There are no other reports of halogens influencing the growth of LaB<sub>6</sub>, which is likely due to assumptions that fast heating rates and high temperatures were required to drive the reaction (at which point any weakly bound halogens would be gone). However, there are examples in the literature where two La atoms in a complex are bridged by Cl [19] or I [20]. In this work we explore the critical role of the anion of the lanthanum precursor in growth of LaB<sub>6</sub>, and how the physical chemistry of the anion influences lattice forma-

tion. We perform a controlled study of this by focusing on reactions with relatively slow crystal growth (lower temperature reactions), which make the small nuances of nucleation and growth easier to observe.

### 4.1. Influence of Cl anion on LaB<sub>6</sub> growth (via in-situ diffraction)

The lanthanum salt and sodium borohydride precursors of the solid state LaB<sub>6</sub> synthesis have several diffraction peaks close to or completely overlapping with those of LaB<sub>6</sub>. In order to make these fine distinctions and to understand the reaction progress, a control study was necessary to evaluate whether or not LaB<sub>6</sub> diffraction peaks would be distinguishable from the heated reactants. A LaCl<sub>3</sub>/NaBH<sub>4</sub> mixture was quickly heated (5 °C/s) to 600 °C, and the diffraction measured. As expected, all diffraction peaks from the precursors shifted slightly to lower 2-Theta (due to lattice expansion) with increasing heat. By 600 °C the three close peaks of LaCl<sub>3</sub> at about 13.5° disappeared, suggesting all of the starting LaCl<sub>3</sub> was consumed, and new diffraction peaks appeared at about 9.8° and 13.9° (Fig. 1A). When magnifying the diffraction pattern at 600 °C the peaks of LaB<sub>6</sub> were clearly visible and found to align closely with the NIST-LaB<sub>6</sub> standard at the same temperature (Fig. 1B), confirming the feasibility of situ diffraction measurements. The (1 1 0), (1 1 1), and (2 0 0) lattice planes of LaB<sub>6</sub> were easiest to observe in this study having no overlap with the heated precursors, so these planes are the focus of this publication. To aid the reader in understanding the LaB<sub>6</sub> structure, Fig. 1C illustrates these three planes as they intersect the La atoms within a single unit cell; (1 1 0) includes pairs of La atoms diagonally across the unit cell, (1 1 1) includes three La atoms across the B<sub>6</sub>-B<sub>6</sub> bond, and (2 0 0) includes four La atoms on the face of the unit cell.

To better understand how LaB<sub>6</sub> evolves in the reaction it was important to slow down crystal growth by reducing the rate of heating. A LaCl<sub>3</sub>/NaBH<sub>4</sub> mixture was heated to 600 °C by 0.17 °C/s and diffraction collected every five minutes. To simplify the discussion, we will first focus on the growth of (1 1 0), which is summarized in Fig. 2. As the reaction progressed, the diffraction peaks of LaCl<sub>3</sub> gradually shifted to lower 2-Theta (an expected result due to lattice expansion with heating) until 600 °C, at which point LaCl<sub>3</sub> was completely consumed. At 558 °C the (1 1 0) plane of LaB<sub>6</sub> appeared at 9.75°, so nucleation began before 558 °C. To further explore the influence of Cl on crystal growth, the reaction was repeated with an excess of Cl by adding NaCl as a precursor. Recall that NaCl is a known byproduct of the reaction, so no new metals were introduced. With excess Cl in the system, similar trends were observed (Fig. 2). The diffraction peaks of LaCl<sub>3</sub> shifted to lower 2-Theta (due to lattice expansion) and were again consumed by 600 °C. Interestingly, with an excess of Cl in the reaction, the LaB<sub>6</sub> (1 1 0) plane appeared at least 50 °C sooner than the same reaction without added salt (≤506 °C). Equally interesting is that with excess Cl, the (1 1 0) plane exhibited an obvious shift to higher 2-Theta as the reaction was held at 600 °C, and the appearance of (1 1 0) began at a 2-Theta of 9.66° compared to the 9.83° of the same reaction without Cl. The theory behind why this happens will be described below. It should be noted that larger bridging halogens shift the diffraction peaks to even higher 2-Theta, as is explained for purified LaB<sub>6</sub> nanoparticles in another publication [21]. We focus here solely on in-situ measurements of lattice growth, and for simplicity sake discuss only the use of the Cl halogen.

This traditional solid state method normally heats reactants at much faster rates. Recent results suggested heating rate may be used to control La vacancies and particle size [14a], so we next sought to determine how the heating rate influences LaB<sub>6</sub> growth. A LaCl<sub>3</sub>/NaBH<sub>4</sub>/NaCl mixture was heated to 600 °C by 3 °C/s and diffraction collected every 5 min. The LaCl<sub>3</sub> peaks yet

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