

# Lawrence Berkeley National Laboratory

## LBL Publications

### Title

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

### Permalink

<https://escholarship.org/uc/item/39t905fg>

### Authors

Mattox, Tracy M  
Groome, Chloe  
Doran, Andrew  
et al.

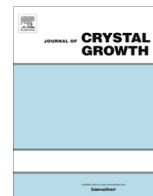
### Publication Date

2018-03-01

### DOI

10.1016/j.jcrysgro.2018.01.013

Peer reviewed



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



Tracy M. Mattox<sup>a,\*</sup>, Chloe Groome<sup>a</sup>, Andrew Doran<sup>b</sup>, Christine M. Beavers<sup>b</sup>, Jeffrey J. Urban<sup>a,\*</sup>

<sup>a</sup> Molecular Foundry, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, CA 94720, USA

<sup>b</sup> Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

## ARTICLE INFO

### Article history:

Received 11 September 2017

Received in revised form 12 January 2018

Accepted 16 January 2018

Available online 31 January 2018

Communicated by R.S. Feigelson

### Keywords:

A1. X-ray diffraction

B1. Nanostructures

B1. Halides

B1. Inorganic compounds

B1. Hexaborides

## 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.

Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 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>.

\* Corresponding authors.

E-mail addresses: [tmmtatx@lbl.gov](mailto:tmmtatx@lbl.gov) (T.M. Mattox), [jjurban@lbl.gov](mailto:jjurban@lbl.gov) (J.J. Urban).

## 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-

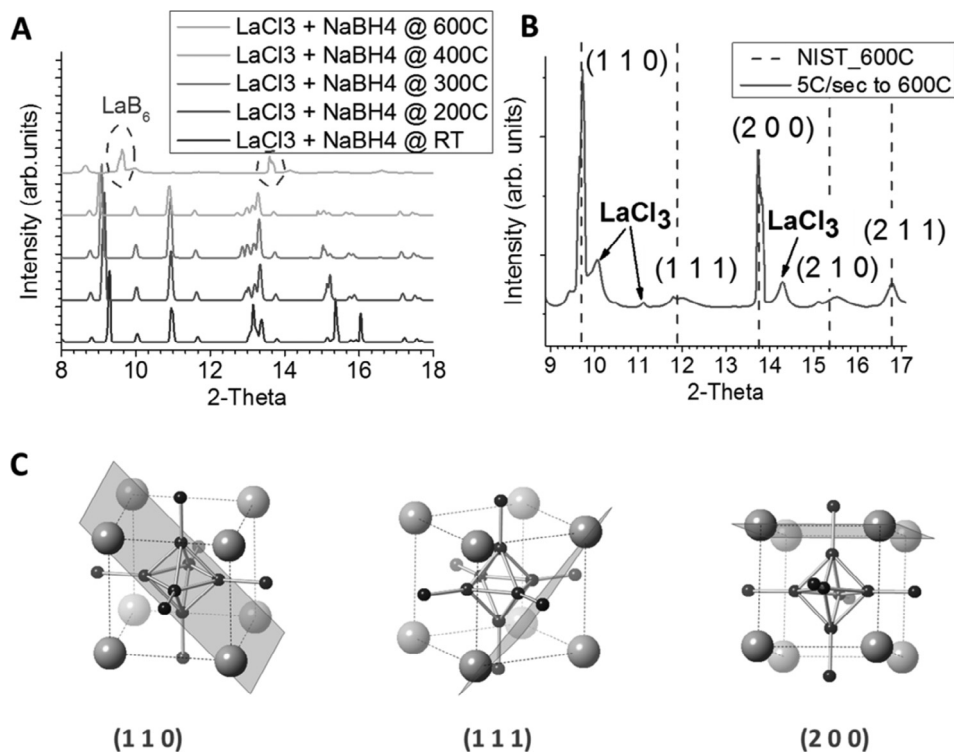
tion. We perform a controlled study of this by focusing on reactions with relatively slow crystal growth (lower temperature reactions), which make the small nuances of nucleation and growth easier to observe.

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

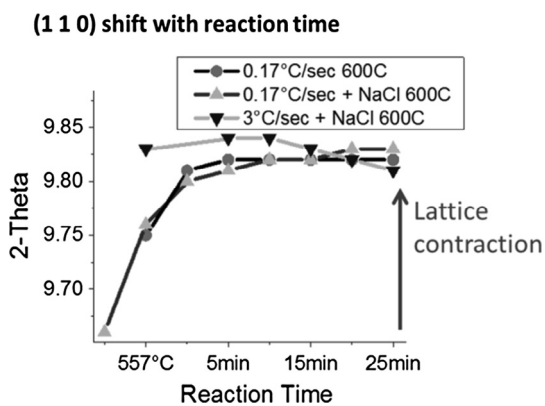
The lanthanum salt and sodium borohydride precursors of the solid state LaB<sub>6</sub> synthesis have several diffraction peaks close to or completely overlapping with those of LaB<sub>6</sub>. In order to make these fine distinctions and to understand the reaction progress, a control study was necessary 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



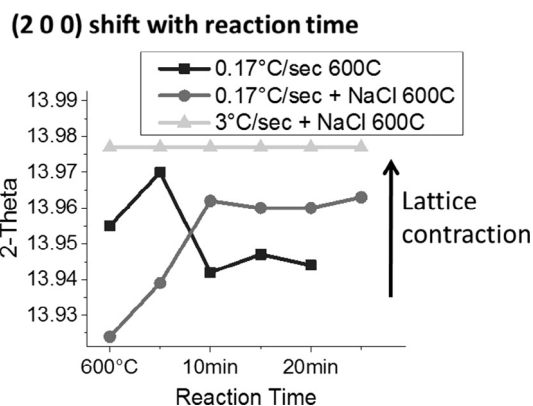
**Fig. 1.** In-situ diffraction pattern of  $\text{LaCl}_3$  and  $\text{NaBH}_4$  (A) heated to various temperatures between room temperature and 600 °C and (B) 600 °C magnified (green solid line) and position of NIST  $\text{LaB}_6$  diffraction peaks at 600 °C (red dashed lines), and (C)  $\text{LaB}_6$  lattice planes (1 1 0), (1 1 1), and (2 0 0). La is grey, B is red, and the lattice plane is blue.



**Fig. 2.** Reaction time versus 2-Theta showing shift of (1 1 0) plane of  $\text{LaB}_6$  as reaction progresses.

again shifted to lower 2-Theta (due to lattice expansion) and by 10 min at 600 °C the  $\text{LaCl}_3$  was consumed. The (1 1 0) plane of  $\text{LaB}_6$  first appeared at 9.84°, when the reaction had been held at 600 °C for 5 min, and continued to shift to lower 2-Theta until the reaction was stopped. Unlike the two slower heating examples, using a quick 3 °C/s rate resulted in the lattice becoming less constrained as the reaction progressed. It's possible that the fast heating causes the crystals to grow so quickly that the effect of Cl is obscured. It is also possible that faster heating does not offer enough time for Cl to continually incorporate within the lattice as the reaction progresses, so the precursors react much faster and continued heating allows particles to grow rather than extending the nucleation stage with slower heating.

The (2 0 0) plane of  $\text{LaB}_6$  shows a slightly different result (Fig. 3). In the 600 °C  $\text{LaB}_6$  reaction (without excess Cl) with slow heating (0.17 °C/s), the (2 0 0) plane first appeared just below



**Fig. 3.** Reaction time versus 2-Theta showing shift of (2 0 0) plane of  $\text{LaB}_6$  as 600 °C reaction progresses.

13.98° as soon as 600 °C was reached. At 5 min of holding at 600 °C, the peak shifted to slightly higher 2-Theta and as the reaction progressed this plane continually shifted to lower 2-Theta, which is indicative of lattice expansion. The initial increase was a result of Cl from the  $\text{LaCl}_3$  incorporating in the structure, but upon depletion of  $\text{LaCl}_3$ , the strain in the structure lessened as the particles grew larger. When excess Cl (via NaCl) was included in the reaction, the (2 0 0) plane first appeared at 13.92° (0.06° less than the reaction without excess Cl) when 600 °C was reached and shifted continually to higher 2-Theta as the reaction progressed, suggesting lattice contraction. Though the data does not allow us to make any firm conclusions, the increased strain with excess Cl is due to one of two reasons: (1) excess Cl extends the nucleation stage and creates more small particles, which have larger lattice strain and/or (2) Cl continues to incorporate into growing particles and creates more bridges between La atoms as the lattice expands. At a faster

**Table 1**  
Summary of diffraction peak movement during in-situ reaction of LaB<sub>6</sub> at 600 °C.

|                 | (1 1 0)                                     | (2 0 0)   |
|-----------------|---|---|
| 0.17 C/s        | Initial contraction<br>No shift with growth | Initial contraction<br>Slight expansion with growth |
| 0.17 C/s + NaCl | Constant contraction                        | Constant contraction                                |
| 3.0 C/s + NaCl  | Constant expansion                          | No shift  |

ramp rate (3 °C/s) with excess Cl, the (2 0 0) plane again appeared as soon as 600 °C was reached, at the same 13.98° position as the slow NaCl-free reaction. With this faster heating the LaCl<sub>3</sub> reacts quickly, so either there is not enough time for excess Cl to coordinate or else the large particle growth has too much of an influence for the effect of Cl to be observed. There was no notable shift in 2-Theta after the initial crystallization was observed.

Table 1 summarizes the shift of the (1 1 0) and (2 0 0) diffraction planes for the 600 °C reactions. With a slow heating rate (0.17 °C/s) both planes show contraction during the nucleation stage, but when held at 600 °C the (1 1 0) plane does not change while (2 0 0) has a slight expansion with continued heating. When salt is incorporated in this slow heating reaction there is a constant contraction of both (1 1 0) and (2 0 0) planes during heating that continues when held at 600 °C. Finally, when the salt-containing reaction is heated at a much faster rate (3.0 °C/s), the (1 1 0) plane constantly expands during heating and at the reaction temperature while the (2 0 0) plane does not shift after it is formed.

The (1 1 1) plane of LaB<sub>6</sub> was difficult to analyze because the diffraction peaks were extremely broad with very low intensity. In a 600 °C reaction heated by 0.17 °C/s, the (1 1 1) plane is only discernible between 506 °C and 600 °C, and in the 3 °C/s reaction LaB<sub>6</sub> was only observed immediately upon achieving 600 °C. In both cases the (1 1 1) plane appeared at 11.83 °C, but no obvious conclusions could be drawn. However, when normalizing the data for the 0.17 °C/s reaction with excess Cl (via NaCl) it was interesting to note that the broad (1 1 1) plane had three overlapping peaks (Fig. 4) that were not present in the other two reactions. When excess Cl was included with the slow ramp rate, the (1 1 1) plane of LaB<sub>6</sub> appeared as a single peak as low as 404 °C, becoming two peaks by 455 °C, and by 600 °C three overlapping peaks were discernible 11.68°, 11.76°, and 11.90°. The (1 1 1) plane was clearly impacted by the incorporation of excess Cl. It's possible that some intermediate phase may be involved or that since there

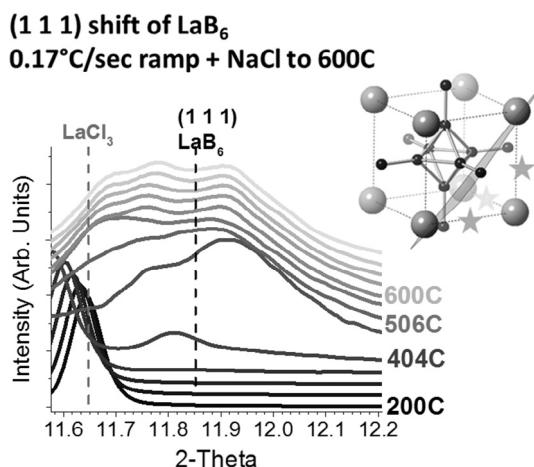
are multiple peaks Cl may incorporate non-uniformly, stretched in multiple directions as the reaction progresses. We were unable to draw any definitive conclusions.

The observations made of the growth of the (1 1 0), (1 1 1), and (2 0 0) planes are intriguing, and the shift of (1 1 1) and (1 0 0) planes to higher 2-Theta as the reaction was held at the reaction temperature was unexpected as heat and particle growth over time typically expand the lattice, causing a shift of the diffraction pattern to lower 2-Theta. This “negative thermal expansion” is quite rare, but there are examples in the literature with a variety of explanations for the effect. For instance, contraction of the lattice with heat results from excess oxygen found in interstitial positions in MgAl<sub>2</sub>O<sub>4</sub> [22], from transverse vibrations of Zr-O-W bonds in ZrW<sub>2</sub>O<sub>8</sub> [23], and as a result of magnetic phase transitions in LaF<sub>11.4</sub>Si<sub>1.6</sub> [24]. Cubic ScF<sub>3</sub> also exhibits this behavior and is explained simply by transverse motions of F between Sc atoms [25]. The structure of ScF<sub>3</sub> is a cube with Sc on each corner and F bridging Sc atoms along the edge of the unit cell, and although the structure differs from LaB<sub>6</sub> we suspect the behavior of F between Sc atoms is similar to Cl between La atoms in the LaB<sub>6</sub> system.

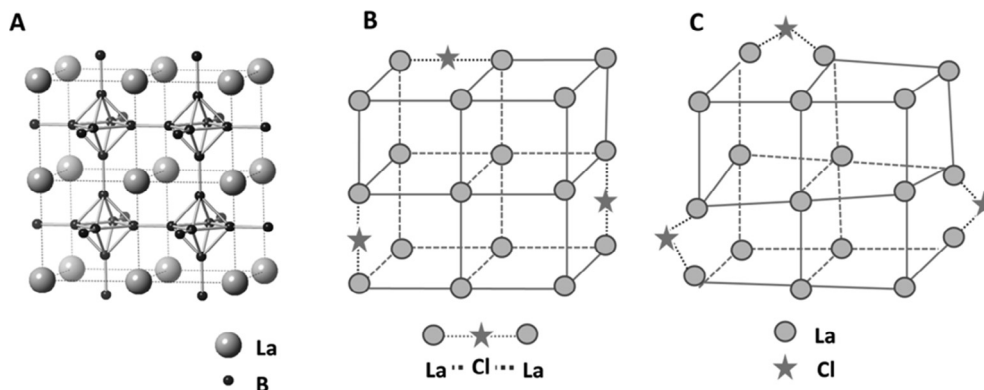
The LaB<sub>6</sub> structure is typically described as sheets of interconnected hexaboride clusters with unbound La atoms in the interstitial spaces (Fig. 5A), and this arrangement of boron traps La atoms in the corner positions of a cube. The knowledge that Cl must be bound in the structure, that the (1 1 0) and (2 0 0) planes contract during growth with an excess of Cl, and that the (1 1 1) plane becomes multiple peaks with excess Cl lead us to the conclusion that Cl acts as a bridging ligand between La atoms on the edge of the unit cell. This is depicted in Fig. 5B (omitting boron for clarity). As the heating of LaB<sub>6</sub> continues, the bound Cl atoms start to pull away from the structure and the La–Cl–La bonds act as a spring, much the same as that described for ScF<sub>3</sub> [25], with transverse motions between Cl and La. Heating forces Cl to move away from the connecting La atoms, which brings the La atoms closer together. This in turn increases strain and causes the lattice to contract (Fig. 5C). This effect was only observed with slow heating rates, so quick heating either does not allow enough time for Cl to bind or else the growth of the particles is fast enough to hide the effect Cl has on growth.

It is interesting that Cl has such a strong influence on the LaB<sub>6</sub> synthesis, and this knowledge may easily lead to new avenues of research. The excess Cl in the structure adds more electrons to an already electron-dense system, which is uncommon as charge compensation usually drives attraction of cations; this unusual behavior naturally motivates further study of the electronic and plasmonic properties of LaB<sub>6</sub>. Since we now know it's possible for an atom to bridge La in this system, it may also be possible for La to bind to small molecules just on the surface, via chemisorption, which may enable new possibilities for catalysis of refractory or multi-electron reductions. Furthermore, a stable ligand with a dangling Cl may be able coordinate with La to make particles soluble for direct film applications, or a molecule with specific properties could be added to enhance the already intriguing properties. More work is needed to fully understand the mechanism of formation to determine if such applications may be feasible, but it is clear from this study that gaining more control over LaB<sub>6</sub> is possible.

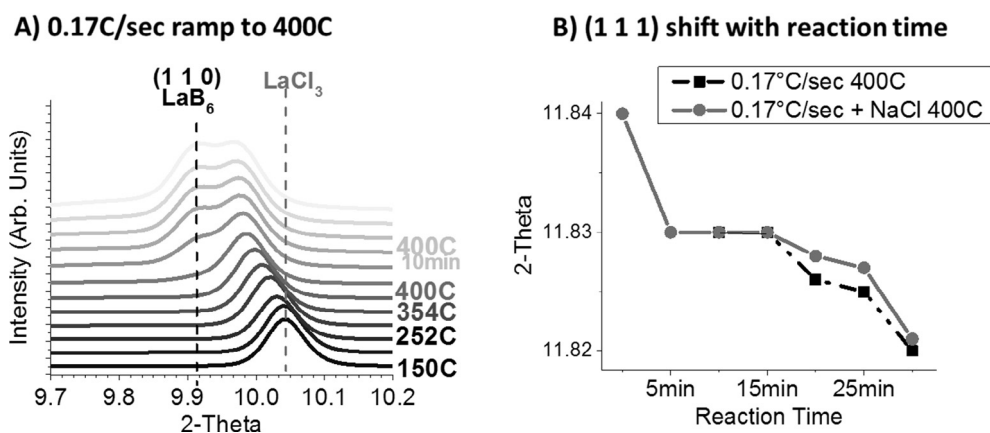
While adjusting the heating rate offers a knob to control Cl incorporation in the LaB<sub>6</sub> lattice in a 600 °C reaction, the heating rate also offers control over La vacancies when the reaction temperature is between the melting point (400 °C) and decomposition temperature (500 °C) of NaBH<sub>4</sub> [14a]. In this temperature range it is easiest to fine tune and control the particle size and stoichiometry of the final product. Quick reactions between 400 °C and 500 °C with fast heating rates create more La vacancies, while slow



**Fig. 4.** Formation of LaB<sub>6</sub> (1 1 1) plane when increasing the reaction temperature from 200 °C to 600 °C (peaks normalized). Inset image displays a single unit cell of LaB<sub>6</sub> showing where excess Cl atoms (star) might link La atoms (large spheres = La, small spheres = B).



**Fig. 5.** Four unit cells of A)  $\text{LaB}_6$ , B) La positions and select theorized Cl positions in  $\text{LaB}_6(\text{Cl})$  (boron omitted for clarity and the grey lines between La atoms are NOT bonds, but aid in viewing their position), and C) the theorized image depicting how removal of Cl with heating brings La atoms closer together before relaxing into normal  $\text{LaB}_6$  framework.



**Fig. 6.** The (1 1 0) lattice plane of  $\text{LaB}_6$  observed during in-situ diffraction study of  $\text{LaB}_6$  synthesis from 150 °C to 400 °C heated at a rate of 0.17 °C/s (peaks normalized) and B) the shift of and (1 1 1) with and without excess Cl via NaCl.

heating produces stoichiometric  $\text{LaB}_6$ . Given our new insight into the growth of  $\text{LaB}_6$  coupled with the knowledge that lower temperatures offer more control, we were curious to see how the  $\text{LaB}_6$  lattice evolves around the melting point of  $\text{NaBH}_4$ . We know from the same previous study that regardless of the heating rate, higher temperatures yield stoichiometric samples, which is the case for the 600 °C reactions already mentioned. Since an in situ diffraction study can't directly observe La vacancies, we chose to be consistent with the stoichiometry and used only a slow ramp rate for lower temperature reactions.

#### 4.2. Influence of reduced reaction temperature on $\text{LaB}_6$ growth (via in-situ diffraction)

A  $\text{LaCl}_3/\text{NaBH}_4$  mixture was heated by 0.17 °C/s to 400 °C and data collected every 5 min. The diffraction of  $\text{LaCl}_3$  shifted as expected to lower 2-Theta (due to lattice expansion), but was not completely consumed throughout the reaction. As a result, nucleation continued to occur with additional heating and particles remained small (hence the broad diffraction peaks) rather than growing into large bulk sizes. The (1 1 0) plane appeared at 9.91° after heating for ten minutes at 400 °C, and as the reaction progressed the intensity increased but no peak shift was observed. The (1 1 1) plane of  $\text{LaB}_6$  appeared at 11.82° at the same ten minute time, and also gained in intensity with only a slight shift to lower 2-Theta as the reaction progressed. The (2 0 0) plane appeared at 14.02° and increased in intensity with no peak shift as the reaction

progressed. Unfortunately, the addition of NaCl obscured the (1 1 0) and (2 0 0) planes. However, the (1 1 1) plane became obvious at 11.84° immediately upon reaching 400 °C, 10 min sooner than the salt-free reaction, and shifted to lower 2-Theta with continued heating. This suggests that the nucleation of  $\text{LaB}_6$  occurred more quickly when excess Cl was available. The shift of the (1 1 1) plane to lower 2-Theta with and without additional Cl is (Fig. 6B) is a result of Cl availability, where the low temperature slows the reaction of  $\text{LaCl}_3$  and NaCl simply adds more Cl. This result is again indicative of Cl bridging La atoms, and the lattice strain increases in the same manner as was observed in the higher temperature reactions.

Though the exact reaction mechanism has yet to be discovered, it is clear that the Cl in this solid state method has an important role and that the bridging Cl atoms offer new means of control that were previously unexplored. With slow heating rates, excess Cl speeds the rate of the reaction, allowing crystallization to start much sooner. The use of excess Cl also provides control over lattice strain and electron density within the system, possibly opening many new doors for new research in this field.

## 5. Conclusion

In conclusion, in situ diffraction data was collected as  $\text{LaB}_6$  crystal growth progressed and the evolution of the individual (1 1 0), (1 1 1), and (2 0 0) lattice planes was observed. The data supports the theory that bridging Cl exists between La atoms within  $\text{LaB}_6$ ,

and shows that Cl has a strong influence on crystal growth – especially when a slow heating rate is used. Though previously unexplored, introducing excess Cl into the reaction forces crystallization to occur more quickly and at lower temperatures with a slow heating rate. Additionally, excess Cl causes the lattice to contract with reaction progression even after the  $\text{LaCl}_3$  precursor has been consumed. Though the same shift was not observed at higher temperatures, it's possible that the shift of diffraction peaks due to the much larger particle sizes which form at higher temperatures prevented the influence of Cl from being observed.

This work helps us gain a better understanding of how  $\text{LaB}_6$  grows, and may help researchers find better methods to design and control the properties of  $\text{LaB}_6$  to meet their application needs. For instance, in knowing how to expand the lattice during heating it may be possible to incorporate other ions or metal dopants in-situ rather than attempting to do so post-synthesis. This would offer one more option for tuning the plasmonic properties of  $\text{LaB}_6$ . The ability of halogens to incorporate and influence this reaction is intriguing, and it's very possible that this applies to other reactions. For instance, other ceramics and refractory materials might be influenced by the inclusion of excess halogens during the synthesis, but these materials are typically heating above  $1500^\circ\text{C}$ , at which point any weakly bound bridging atoms would be gone. These results may spur on research in other fields that did not previously consider the influence of the anions of their precursors, opening new avenues of study in a variety of synthetic fields.

## Acknowledgements

We would like to thank Dr. Tevye Kuykendall for his helpful discussions. This work was supported by the Molecular Foundry and the Advanced Light Source at Lawrence Berkeley National Laboratory, both user facilities supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy (DOE) under Contract No. DE-AC02-05CH11231. Work was also supported in part by the DOE Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Science Undergraduate Laboratory Internship (SULI) program.

## Notes

The authors declare no competing financial interests.

## References

- [1] H. Zhang, J. Tang, Q. Zhang, G. Zhao, G. Yang, J. Zhang, O. Zhou, L.-C. Qin, Field emission of electrons from single  $\text{LaB}_6$  nanowires, *Adv. Mater.* 18 (1) (2006) 87–91.
- [2] S. Zhou, J. Zhang, D. Liu, Z. Lin, Q. Huang, L. Bao, R. Ma, Y. Wei, Synthesis and properties of nanostructured dense  $\text{LaB}_6$  cathodes by arc plasma and reactive spark plasma sintering, *Acta Mater.* 58 (15) (2010) 4978–4985, <https://doi.org/10.1016/j.actamat.2010.05.031>.
- [3] L. Xiaoa, Y. Sub, W. Qjud, Y. Liua, J. Rand, J. Wua, F. Lua, F. Shaod, D. Tangc, P. Peng, Solar radiation shielding properties of transparent  $\text{LaB}_6$  filters through experimental and first-principles calculation methods, *Ceram. Int.* 42 (12) (2016) 14278–14281, <https://doi.org/10.1016/j.ceramint.2016.05.105>.
- [4] L. Bao, L. Chao, W. Wei, O. Tegus, Tunable transmission light in nanocrystalline  $\text{La}_{1-x}\text{Eu}_x\text{B}_6$ , *Mater. Lett.* 139 (2015) 187–190, <https://doi.org/10.1016/j.matlet.2014.10.060>.
- [5] L. Xiao, Y. Su, X. Zhou, H. Chen, J. Tan, T. Hu, J. Yan, P. Peng, Origins of high visible light transparency and solar heat-shielding performance in  $\text{LaB}_6$ , *Appl. Phys. Lett.* 101 (2012) 041913–1–041913–3, <https://doi.org/10.1063/1.4733386>.
- [6] T.M. Mattox, S. Chockkalingam, I. Roh, J.J. Urban, Evolution of vibrational properties in lanthanum hexaboride nanocrystals, *J. Phys. Chem. C* 120 (9) (2016) 5188–5195.
- [7] Y. Li, N. Zhong, Q. Liao, Q. Fu, Y. Huang, X. Zhu, Q. Li, A biomaterial doped with  $\text{LaB}_6$  nanoparticles as photothermal media for enhancing biofilm growth and hydrogen production in photosynthetic bacteria, *Int. J. Hydrogen Energy ASAP* (2017) 1–11.
- [8] H. Zhang, Q. Shang, J. Tang, L.-C. Qin, Single-crystalline  $\text{LaB}_6$  nanowires, *J. Am. Chem. Soc.* 127 (9) (2005) 2862–2863, <https://doi.org/10.1021/ja043512c>.
- [9] J.R. Brewer, N. Deo, Y.M. Wang, C.L. Cheung, Lanthanum hexaboride nanoobelisks, *Chem. Mater.* 19 (2007) 6379–6381.
- [10] D.J. Late, S. Karmakar, M.A. More, S.V. Bhoraskar, D.S. Joag, Arc plasma synthesized  $\text{LaB}_6$  nanocrystallite film on various substrates as a field emitter, *J. Nanopart. Res.* 12 (7) (2010) 2393–2403.
- [11] M. Zhang, L. Yuan, X. Wang, H. Fan, X. Wang, X. Wu, H. Wang, Y. Qian, A low-temperature route for the synthesis of nanocrystalline  $\text{LaB}_6$ , *J. Solid State Chem.* 181 (2) (2008) 294–297.
- [12] T.M. Mattox, A. Agrawal, D.J. Milliron, Low temperature synthesis and surface plasmon resonance of colloidal lanthanum hexaboride ( $\text{LaB}_6$ ) nanocrystals, *Chem. Mater.* 27 (2015) 6620–6624, <https://doi.org/10.1021/acs.chemmater.5b02297>.
- [13] (a) L. Pengting, L. Chong, N. Jinfeng, O. Jun, L. Xiangfa, Growth and design of  $\text{LaB}_6$  microcrystals by aluminum melt reaction method, *Cryst. Eng. Comm.* 15 (2013) 411–420; (b) L. Chao, L. Bao, W. Wei, O. Tegus, Z. Zhang, Effects of nanoparticle shape and size on optical properties of  $\text{LaB}_6$ , *Plasmonics* 11 (2016) 697–701.
- [14] (a) C. Groome, I. Roh, T.M. Mattox, J.J. Urban, Influence of size and structural defects on the vibrational properties of lanthanum hexaboride nanocrystals, *ACS Omega* (2017); (b) M.J. McKelvy, L. Eyring, E.K. Storms, Analytical and structural analysis of the lanthanum-deficient lanthanum hexaboride, *J. Phys. Chem.* 88 (9) (1984) 1785–1790, <https://doi.org/10.1021/j150653a024>; (c) V. Paderno, Y. Paderno, V. Britun, Features of the real structure of lanthanum hexaboride single crystals, *J. Alloys Compd.* 219 (1–2) (1995) 228–231, [https://doi.org/10.1016/0925-8388\(94\).05051-1](https://doi.org/10.1016/0925-8388(94).05051-1).
- [15] Y. Yuan, L. Zhang, L. Liang, K. He, R. Liu, G. Min, solid-state reaction route to prepare  $\text{LaB}_6$  nanocrystals in vacuum, *A Ceram. Int.* 37 (2011) 2891–2896.
- [16] (a) J.M. Lafferty, Boride cathodes, *J. Appl. Phys.* 22 (1951) 299–309, <https://doi.org/10.1063/1.1699946>; (b) J.R. Rea, E. Kostiner, The formation of calcium and certain rare-earth hexaboride single crystals, *J. Cryst. Growth* 11 (1971) 110–112.
- [17] C. Prescher, V.B. Prakapenka, DIOPTAS: a program for reduction of two-dimensional X-ray diffraction data and data exploration, *High Press. Res.* 35 (3) (2015) 223–230, <https://doi.org/10.1080/08957959.2015.1059835>.
- [18] A. Doran, L. Schlicker, C.M. Beavers, S. Bhat, M.F. Bekheet, A. Gurlo, Compact low power infrared tube furnace for in situ X-ray powder diffraction, *Rev. Sci. Instrum.* 88 (2017) 013903, <https://doi.org/10.1063/1.4973561>.
- [19] (a) J. Ren, J. Guan, S. Jin, Synthesis and X-ray structure of an organolanthanum complex  $[(\text{Bu}^i\text{Cp})_3\text{LaClLi}(\text{THF})_3]$ , *Polyhedron* 13 (21) (1994) 2979–2982; (b) H. Shen, H.-S. Chan, Z. Xie, Synthesis and structural characterization of constrained-geometry organolanthanide chlorides and alkyls incorporating the ligand  $[\text{n}^5\text{-(C}_9\text{H}_6\text{)}(\text{C}_2\text{B}_{10}\text{H}_{10})_2\text{-}]$ , *Organometallics* 27 (2008) 5309–5316.
- [20] M. Lulei, J.D. Martin, L.M. Hoistad, J.D. Corbett, The closely related structure types with unprecedented biotetrahedral rare-earth-metal clusters centered by transition metals:  $\text{A}_2\text{R}_{10}\text{I}_7\text{Z}_2$  (A = Rb, Cs; R = La, Ce, Pr; Z = Co, Ni, Ru, Os) and  $\text{La}_{10}\text{I}_{15}\text{Os}_2$ , *J. Am. Chem. Soc.* 119 (1997) 513–520.
- [21] Tracy M. Mattox, C. Groome, Andrew Doran, Christine M. Beavers, J. Jeffrey, Urban, anion-mediated negative thermal expansion in lanthanum hexaboride, *Solid State Commun.* (2017), <https://doi.org/10.1016/j.ssc.2017.07.012> (in press).
- [22] K.C. George, S. Kurien, J. Mathew, Lattice strain and lattice expansion of nanoparticles of  $\text{MgAl}_2\text{O}_4$  as a function of particle size, *J. Nanosci. Nanotechnol.* 7 (6) (2007) 2016–2019.
- [23] J.S.O. Evans, T.A. Mary, T. Vogt, M.A. Subramanian, A.W. Sleight, Negative thermal expansion in  $\text{ZrW}_2\text{O}_8$  and  $\text{HfW}_2\text{O}_8$ , *Chem. Mater.* 8 (1996) 2809–2823.
- [24] F.-X. Hu, B.-G. Shen, J.-R. Sun, Z.-H. Cheng, G.-H. Rao, X.-X. Zhang, Influence of negative lattice expansion and metamagnetic transition on magnetic entropy change in the compound  $\text{LaF}_{11.4}\text{Si}_{1.6}$ , *Appl. Phys. Lett.* 78 (2001) 3675–3679, <https://doi.org/10.1063/1.1375836>.
- [25] C.W. Li, X. Tang, J.A. Munoz, J.B. Keith, S.J. Tracy, D.L. Abernathy, B. Fultz, Structural relationship between negative thermal expansion and quartic anharmonicity of cubic  $\text{ScF}_3$ , *PRL* 107 (2011) 195504–1–195504–4.