Hexaborides: a review of structure, synthesis and processing

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Abstract

Hexaboride compounds are a subset of borides with many interesting thermal, electrical, magnetic and physical properties. As such, interest has grown in this class of ceramics not only to understand their peculiar characteristics, but also to apply them to modern scientific and engineering problems. Hexaborides are currently used or show promise for a variety of applications such as electron emitters, thermoelectric materials, coatings, single-photon detectors and superconductors. A shared crystal structure amongst all hexaborides permits them to readily form solid solutions, allowing for fine-tuning of electrical, optical and thermal properties with mixed-metal compounds. Recent advances in characterization techniques have allowed researchers to gain new insights and renewed interest in some of the more exotic hexaboride behaviors such as surface conductivity in SmB$_6$ or magnetic ordering in CeB$_6$. Like many other non-oxide ceramics, borides present certain synthesis and processing challenges. This paper presents an overview of the structure, synthesis and processing of hexaboride compounds in an effort to guide researchers with the first step in pursuing these interesting and unique materials.

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Olivia A. Graeve, Ph.D. Prof. Graeve joined the University of California, San Diego, in 2012, and is currently Professor in the Department of Mechanical and Aerospace Engineering, Director of the CaliBaja Center for Resilient Materials and Systems, and Faculty Director of the IDEA Engineering Student Center. Prof. Graeve holds a Ph.D. in Materials Science and Engineering from the University of California, Davis, and a Bachelor’s degree in Structural Engineering from the University of California, San Diego. Her area of research focuses on the design and processing of new materials for extreme environments, including extremes of temperature, pressure, and radiation. Prof. Graeve has been involved in many activities related to the recruitment and retention of women and Hispanic students in science and engineering and has received several prestigious awards including the National Science Foundation CAREER award, the 2006 Hispanic Educator of the Year award by the Society of Hispanic Professional Engineers, the 2010 Karl Schwartzwalder Professional Achievement in Ceramic Engineering Award by the American Ceramic Society, the 2012 B.J. Harrington Lectureship by McGill University, the 2011 Society of Hispanic Professional Engineers “Jaime Oaxaca” Award, Outstanding Engineering Educator by the San Diego Chapter of the California Society of Professional Engineers (2015), Alumna of the Year by Southwestern College (2015), Hispanic Engineer National Achievement Educator Award (2017), and SHPE Innovator Award (2017). More recently, she has been inducted into the Tijuana Walk of Fame (2014) and to the Mexican Academy of Engineering (2016), and has been named Fellow of the American Ceramic Society (2017). In addition, Forbes Magazine named her one of the 100 Most Powerful Women of Mexico (2017).

1. Introduction

Borides represent a multitude of compounds found in many modern engineering applications and whose unique properties stem from their crystal structure and bonding. The covalent bonding between the boron atoms is very strong, providing the materials with high hardness and high melting temperatures. Although there are various borides that display high hardness [1–3], hexaborides are not often considered for their mechanical properties. Nevertheless, there is research documenting the elastic modulus [4,5], flexural strength [6,7], and hardness [4,6,8–10] of various hexaboride compounds.

Electronic conductivity is where hexaboride compounds really begin to display their unique range of properties. This stems almost directly from the bonding of the M6B6 structure, in which the covalently-bonded boron atoms “trap” the metal atom, the main purpose of which is to donate electrons to the charge deficient boron sublattice. The number of donated electrons has been experimentally and theoretically determined to be two [11,12], making divalent hexaborides semiconductors and trivalent hexaborides metallic [13–15]. LaB6 is one of the most well-known trivalent hexaboride compounds and is frequently used as a thermionic electron emitter due to its low work function (2.6 eV) and low vapor pressure at high temperature [16,17]. The unusually high conductivity of divalent alkaline-earth hexaborides has been described in terms of both overlapping band gaps and carrier concentration, with the influence of impurities and metal vacancies being quite apparent in experimental results, in which very low levels of doping or impurities (0.5%) can cause divalent compounds to exhibit metallic behavior [18–20]. This phenomenon has also been explained by more recent band gap calculations showing that the changes in B–Bmura and B–Bminter distances can easily affect the electronic properties, resulting in slight band overlapping and a shift from semiconducting to semi-metallic behavior [21–23]. This range of electrical conductivity values gives rise to the potential for hexaborides to be used as thermoelectric materials. In particular, alkaline-earth hexaborides have shown promise as possible n-type equivalents with good Seebeck coefficients [24,25]. Although the effect of doping on these materials can often lead to a higher than desirable electrical conductivity, it has not diminished investigations on hexaborides for thermoelectric applications, especially on the divalent candidates SrB6, CaB6, BaB6 and their alloys [24–26]. There is also evidence from CaB6–SrB6 diffusion couples that the metal cations can diffuse through the boron sublattice under the influence of an electric current [27] during spark plasma sintering. Mixed-valent compounds such as SmB6 have garnered great interest as Kondo insulators. In particular, the high temperature metallic state of SmB6 evolves into an insulator at low temperatures and experimental evidence suggests its potential as a topological insulator [28–33]. Like other borides such as MgB2, hexaborides can display superconducting properties with a surprisingly high critical temperature (Tc) of 8.4 K for YB6 [34,35]. Unlike the high energy (60 meV) coupled mode of MgB2, YB6 lies at significantly lower energy (8 meV), which has been attributed to the vibration of Y atoms in the boron sublattice [34].

Magnetism in hexaborides is an intriguing phenomenon and recent research has been aimed at determining the source of these properties. Magnetic ordering in EuB6 has been attributed to the ferromagnetic alignment of localized Eu 4f electron moments [36]. Specific heat and magnetization measurements reveal that this state is reached via two distinct transitions, with the first representing the Curie temperature at TC = 12.6 K and the second representing a charge delocalization transition caused by the overlap of magnetic polarons and resulting in colossal magnetoresistance at TM = 15.5 K [37,38]. Pure CeB6 displays three distinct magnetic phases starting with antiferromagnetic (phase III) in zero field at the lowest temperatures, followed by an antiferroquadrupolar phase (phase II) at TN = 2.4 K, and finally a paramagnetic state (phase I) above TN = 3.2 K [39–41]. The review by Cameron et al. [41] delves into the intricacies of the low-temperature magnetic ordering in CeB6, as well as the lanthanum-doped versions of Ce1–xLaxB6, and depicts just how complex and elusive this phenomenon is.

Although there are many interesting properties exhibited by hexaboride compounds, the first step for the study of any material must be producing it. Along with an overview of the structure and bonding, this review focuses on the history and recent advances concerning the synthesis and processing of hexaboride compounds.
2. Structure and bonding

The most recognizable feature of hexaborides is their cubic crystal structure, one shared by all compounds with the MB₆ stoichiometry. Commonly referred to as the CaB₆ prototype structure, the lattice is composed of a single metal atom surrounded by eight octahedra of boron atoms, each centered on a corner of the cube (Fig. 1) and of Pm₃m symmetry. Particles of these materials also easily take on cubic form (Fig. 2), thus mirroring the crystal structure. Each boron atom has a coordination of 5, with 4 adjacent in the octahedra and another along one of the cube axes. The metal atoms at the center are coordinated by 24 boron atoms, between which no valence bonds appear to exist [13,14,42–44]. On the other hand, the boron atoms are covalently bonded to each other and responsible for many of the physical and chemical properties exhibited by these materials [13]. Because each boron atom must distribute its 3 valence electrons over 5 bonds, the cubic boron sublattice itself is inherently electron deficient and cannot exist without donated electrons from the metal atoms. Although hexaborides must have a metal cation with a charge of at least +2 to be electronically stable [11,12], metal-deficient KB₆ has been produced in controlled environments [45,46]. This concept, coupled with the fact that the boron sublattice forms a semi-rigid “cage”, limits the metal atom candidates based on size and valency to alkaline-earth metals, rare-earth metals and some actinide metals. As seen in Table 1, the lattice parameters do not significantly vary between metal hexaborides, suggesting that the boron framework is the primary contributor to the unit cell size. Because the lattice parameters of the hexaboride compounds are so similar, they readily form solid solutions with one another, with the largest and smallest lattice parameters only differing by 4% (a = 0.4093 nm for ThB₆ and a = 0.4262 nm for BaB₆) [22]. Some of the studies detailing the properties of mixed-metal (M¹⁻M²)B₆ compounds include (La-Y)B₆ [47], (La-Ba)B₆ [47], (La-Eu)B₆ [15,47], (La-Ce)B₆ [48,49], (La-Na)B₆ [50], (Eu-Y)B₆ [47], (Eu-Ba)B₆ [47], (Ca-Sr)B₆ [25,26,51], (Ca-Ba)B₆ [26,51], (Sr-Ba)B₆ [26,51], (Ca-Yb)B₆ [25], and (Ca-Sm)B₆ [25], among others. With a few exceptions [47,51], these studies all report homogenous solid solutions and an even distribution of the two metal atoms throughout the boron sublattice. The formation of nano-domains in mixed-metal hexaborides rich in either M¹ or M² has been observed in (Ca-Ba)B₆ and (Sr-Ba)B₆ powders produced by combustion synthesis, but not in (Ca-Sr)B₆ powders produced by the same method [51]. This phenomenon was found to be metastable and was attributed to the size difference between the two metal cations and the nature of the combustion synthesis process used to produce the powders, which is quite rapid and introduces preferential formation during the chemical reaction. Olsen and Cafiero [47] also found a negative deviation from Vegard’s law in their (La-Eu)B₆ samples, which they attributed to the compressibility of the larger EuB₆ constituent, but noted solid solutions over the entire compositional range for all ternary materials, except those containing Y²⁺, which produced a mixture of MB₆ and YB₄ crystals. The negative deviation from Vegard’s law reported in (La-Eu)B₆ samples is curious, and without reported X-ray diffraction patterns it is difficult to determine if this is, in fact, due to compressibility of the EuB₆ or an artifact of peak asymmetry similar to that seen in mixed alkaline-earth hexaboride compounds [51].

The general thermal stability of metal hexaborides is based on two main factors: (1) the saturation vapor pressure of the metal cation and (2) the stability of the bonds in the boron sublattice [13]. The greater the saturation vapor pressure of the metal, the greater the volatility and ability of the atom to dissociate from the structure. While there is little information on the surface termination of metal hexaborides, Schmidt et al. [42] used density functional theory (DFT) to show that segregated regions of metal and boron-terminated surfaces produce the lowest energies for CaB₆, SrB₆, and BaB₆, while the trivalent LaB₆ minimizes the surface energy by arranging the La ions in parallel rows on the surface. X-ray photoelectron spectroscopy measurements suggest regions with mixed surface terminations for CaB₆ and SrB₆ and a B-rich surface for BaB₆.
Table 1 – Summary of experimental structural parameters for metal hexaborides (adapted from Mackinnon et al. [22]).

<table>
<thead>
<tr>
<th>MB₆</th>
<th>a (Å)</th>
<th>B-B₆ (Å)</th>
<th>B-B₁₂ (Å)</th>
<th>M-B (Å)</th>
<th>Rᵥ (%)</th>
<th>B site occupancy</th>
<th>M site occupancy</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>KB₆</td>
<td>4.2246</td>
<td>1.8033</td>
<td>1.6744</td>
<td>3.1023</td>
<td>2.2</td>
<td>1.0</td>
<td>0.947</td>
<td>0.1982</td>
</tr>
<tr>
<td>CaB₆</td>
<td>4.1514</td>
<td>1.7520</td>
<td>1.6760</td>
<td>3.0528</td>
<td>5.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.2019</td>
</tr>
<tr>
<td>SrB₆</td>
<td>4.1953</td>
<td>1.7620</td>
<td>1.7040</td>
<td>3.0865</td>
<td>2.1</td>
<td>1.0</td>
<td>1.0</td>
<td>0.2031</td>
</tr>
<tr>
<td>YB₆</td>
<td>4.1000</td>
<td>1.7460</td>
<td>1.6300</td>
<td>3.0115</td>
<td>4.4</td>
<td>1.0</td>
<td>1.0</td>
<td>0.1988</td>
</tr>
<tr>
<td>BaB₆</td>
<td>4.2618</td>
<td>1.7800</td>
<td>1.7440</td>
<td>3.1373</td>
<td>2.9</td>
<td>1.0</td>
<td>1.0</td>
<td>0.2047</td>
</tr>
<tr>
<td>LaB₆</td>
<td>4.1569</td>
<td>1.7660</td>
<td>1.6590</td>
<td>3.0542</td>
<td>2.9</td>
<td>1.0</td>
<td>1.0</td>
<td>0.1996</td>
</tr>
<tr>
<td>CeB₆</td>
<td>4.1407</td>
<td>1.7511</td>
<td>1.6644</td>
<td>3.0439</td>
<td>0.8</td>
<td>1.0</td>
<td>1.0</td>
<td>0.2011</td>
</tr>
<tr>
<td>NdB₆</td>
<td>4.1269</td>
<td>1.7574</td>
<td>1.6415</td>
<td>3.0314</td>
<td>1.9</td>
<td>0.979</td>
<td>1.0</td>
<td>0.1982</td>
</tr>
<tr>
<td>SmB₆</td>
<td>4.1346</td>
<td>1.7438</td>
<td>1.6688</td>
<td>3.0381</td>
<td>1.1</td>
<td>1.0</td>
<td>1.0</td>
<td>0.2018</td>
</tr>
<tr>
<td>EuB₆</td>
<td>4.1849</td>
<td>1.7596</td>
<td>1.6964</td>
<td>3.0783</td>
<td>1.3</td>
<td>0.980</td>
<td>1.0</td>
<td>0.2027</td>
</tr>
<tr>
<td>YbB₆</td>
<td>4.1479</td>
<td>1.7525</td>
<td>1.6695</td>
<td>3.0495</td>
<td>1.6</td>
<td>0.977</td>
<td>1.0</td>
<td>0.2012</td>
</tr>
<tr>
<td>ThB₆</td>
<td>4.0931</td>
<td>1.7570</td>
<td>1.6100</td>
<td>3.0045</td>
<td>2.2</td>
<td>1.15</td>
<td>0.997</td>
<td>0.1970</td>
</tr>
</tbody>
</table>

Fig. 3 – Thermal stability of metal hexaborides plotted as saturation vapor pressure vs. lattice parameter. The colors represent the four types of thermal dissociation.

For two MB₆ compounds with the same lattice parameter, such as CaB₆ and LaB₆, the more thermally stable is the one with the least volatile metal (in this case LaB₆). At temperatures immediately below the melting point, hexaborides fall into one of four classes with respect to thermal degradation, as described by Etourneau et al. [13] and illustrated in Fig. 3. As the saturation vapor pressure of the metal atom increases or the radius decreases, the hexaboride stability is reduced. The high stability of Group I hexaborides is due in part to a progressive shrinking of the lattice and the volatility of the metal element increases [13]. On the opposite end, the structural stability also decreases as the lattice parameter increases due to a reduction in strength of the stretched boron-boron bonds. As seen in Fig. 3, the four classes remain distinctly grouped together, allowing one to approximate the thermal degradation behavior based on these two parameters. This is useful in the case of several rare-earth hexaboride compounds that have only recently been synthesized and studied, much later than the original work completed by Etourneau et al. [13].

While there are many examples of compounds changing structure under the influence of high pressures, it was not until 2012 that a high-pressure phase of CaB₆ was discovered by Kolmogorov et al. [52]. The phase transformation was first predicted by DFT, which showed thermodynamic and dynamic instabilities in the CaB₆ structure and a subsequent reduction in Gibbs free energy by transformation to a stable polymorph. This was confirmed experimentally by laser-heating CaB₆ up to 42 GPa while performing in situ X-ray diffraction to observe changes in the crystal structure. Fig. 4 depicts the stable structure (cP7) of CaB₆ [Fig. 4(b)] along with the competing high-pressure structures [Fig. 4(a), (c), and (d)] and the final tetragonal (tI56) structure [Fig. 4(e)]. Han et al. [53] took the DFT analysis a step further to analyze properties of the high-pressure phase and predicted that the bulk, shear and Young’s moduli are larger than that of the low-pressure phase, as well as predicting a reduction in ductility with the transformation to tI56. Understanding the phase transformations in these materials is important if hexaboride compounds find their way into high-pressure applications, or if the tetragonal polymorph could be quenched and stabilized at room temperature.

3. Synthesis

Like many other non-oxide ceramics, including carbides, nitrides and phosphides, the covalently bonded borides are refractory materials with high melting temperatures, thus high synthesis temperatures are often required to produce them. Synthesis of the first boride compounds in the early 19th century was followed closely by the synthesis of the first hexaborides by Moissan and Williams who reduced metal borates with aluminum in an arc furnace to produce CaB₆ and SrB₆ [54]. This process was later refined by Andréix [55], who electrolyzed molten mixtures of metal borates and fluorides. While molten salt electrolysis and solid-state reactions were among the first techniques used to produce hexaborides, they have not become obsolete and are still commonly employed methods today. Although there are many different hexaboride synthesis methods with varying complexities and nuances,
Fig. 4 – Competing high-pressure structures of calcium hexaboride where (a) oP28 (Pnma) is one of the possible distortions of cP7, (b) cP7 (Pm-3 m) is at STP, (c) oS28 (Cmmm) is a metastable structure, (d) oS56 (Cmcm) is our lowest enthalpy structure for 13–32 GPa and (e) is tI56 (I-4mmm) a new ground state candidate above 32 GPa supported by X-ray data [52].

they can all be roughly organized into four basic classifications: (1) solid state, (2) electrolysis and flux, (3) vapor deposition or metal-gas reactions, and (4) combustion or self-propagation. Specific examples for each group are described in this section, however it should be noted that the synthesis of metal hexaborides is not limited to these common methods.

3.1. Solid state reactions

Solid-state reactions are defined here as the mixing of solid precursors and subsequent processing to produce the desired MB$_6$ compound. These techniques require high purity precursors and elevated temperatures, often above 1200 K, where the compound formation occurs as the precursors decompose into their elemental constituents. Any unwanted or excess lighter elements such as H, C, O, N, or B are usually removed as gases. Two of the most popular solid-state methods for synthesizing hexaborides are the borothermal (Eqs 1 and 2) [21,56–61] and carbothermal reductions (Eqs 3 and 4) [62–71]. Borothermal reductions involve a combination of the desired metal oxide and excess boron, while carbothermal reductions utilize carbon or carbon-metal compounds and boron oxide. Boron-carbon reductions (Eqs 5 and 6) use B$_4$C as both the reducing agent (carbon) and boride-former (boron) along with excess boron. Table 2 adapted from Samsonov et al. [72] contains the synthesis temperatures for some common hexaboride compounds using a boron carbide reduction method. The addition of a strong metallic reducing agent, such as Mg, can also be used as the primary reducer [73,74]. As with the carbothermal reduction, B$_2$O$_3$ can be utilized as a boron source as it will be reduced along with the metal oxide (Eqs 7 and 8). Unlike the carbothermal reduction, where the carbon is removed as a gas (CO) during the heating process, the MgO by-product must be removed by chemical means such as an HCl wash.
Table 2 – Synthesis parameters for some metal hexaborides produced by the boron carbide reduction method [72].

<table>
<thead>
<tr>
<th>Hexaboride compound</th>
<th>Reduction temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaB₆</td>
<td>1600</td>
</tr>
<tr>
<td>SrB₆</td>
<td>1500</td>
</tr>
<tr>
<td>BaB₆</td>
<td>1500</td>
</tr>
<tr>
<td>YB₆</td>
<td>1600</td>
</tr>
<tr>
<td>LaB₆</td>
<td>1650</td>
</tr>
<tr>
<td>CeB₆</td>
<td>1600</td>
</tr>
<tr>
<td>PrB₆</td>
<td>1600</td>
</tr>
<tr>
<td>NdB₆</td>
<td>1600</td>
</tr>
<tr>
<td>SmB₆</td>
<td>1650</td>
</tr>
<tr>
<td>EuB₆</td>
<td>1600</td>
</tr>
<tr>
<td>GdB₆</td>
<td>2000</td>
</tr>
<tr>
<td>TbB₆</td>
<td>1800</td>
</tr>
<tr>
<td>YbB₆</td>
<td>1600</td>
</tr>
<tr>
<td>TbB₆</td>
<td>1600</td>
</tr>
</tbody>
</table>

B₂O₃ by-product may be removed through washing (water) or with sufficiently high temperatures so that it vaporizes (>1720 K). Heat treatments under vacuum will cause the B₂O₃ to volatilize at lower temperatures if melting or sintering of the hexaboride phase is a concern.

All relevant chemical reactions, as mentioned above, are:

1. \( \text{M}_2\text{O}_3 + 14\text{B} \rightarrow 2\text{MB}_6 + \text{B}_2\text{O}_3 \) (borothermal)
2. \( 3\text{MO} + 20\text{B} \rightarrow 3\text{MB}_6 + \text{B}_2\text{O}_3 \) (borothermal)
3. \( \text{M}_2\text{O}_3 + 6\text{B}_2\text{O}_3 + 21\text{C} \rightarrow 2\text{MB}_6 + 21\text{CO} \) (carbothermal)
4. \( \text{MO} + 3\text{B}_2\text{O}_3 + 10\text{C} \rightarrow \text{MB}_6 + 10\text{CO} \) (carbothermal)
5. \( \text{M}_2\text{O}_3 + 3\text{B}_4\text{C} \rightarrow 2\text{MB}_6 + 3\text{CO} \) (boron carbide reduction)
6. \( \text{MO} + \text{B}_4\text{C} + 2\text{B} \rightarrow \text{MB}_6 + \text{CO} \) (boron carbide reduction)
7. \( \text{M}_2\text{O}_3 + 6\text{B}_2\text{O}_3 + 21\text{Mg} \rightarrow 2\text{MB}_6 + 21\text{MgO} \) (magnesium reduction)
8. \( \text{MO} + 6\text{B}_2\text{O}_3 + 19\text{Mg} \rightarrow 2\text{MB}_6 + 19\text{MgO} \) (magnesium reduction)

The combination of metals or metal oxides with boron can be a highly exothermic process, and the reaction may begin to self-sustain at temperatures as low as 473 K [75]. Fig. 5 [71] depicts X-ray diffraction patterns of the Ca and B precursors gradually turning into CaB₆ with increasing time at 1473 K. The phase purity of an MB₆ reduction is not always certain and the process may result in either unreacted precursors or undesirable secondary phases. The purity of the precursors, precursor ratio, level of mixing, precursor particle size and reduction temperature profile can all affect the outcome of the process. Complete reduction to the MB₆ phase is more likely to be achieved with small (sub-micron), well-mixed, high-purity precursors that are held at an adequately high temperature for a substantial (>1 h) amount of time. Reduction of metal oxides to the MB₆ phase outside of these conditions is certainly possible, but may be accompanied by residual boron, carbon or metal oxide.

Hexaboride compounds can also be synthesized by a direct reaction of ultra-high purity metal and boron, which are mixed together and heated in a crucible (all under an inert atmosphere) to the boiling temperature of the metal for several hours, to ensure homogeneous mixing [14,26,45,46]. This produces hexaboride compounds of purity corresponding to that of the elemental precursors, however, it is not often used due to the reactivity of the metal precursors with oxygen. The floating zone method utilizes pure metal or metal oxide precursors mixed with excess boron and melted under argon to form precursor rods, which are then heated under vacuum and then cooled to crystallize the material. A similar method called zone leveling uses a zone with a temperature and composition on an adjacent liquidus line that is then moved to precipitate crystals out of the molten solution. Floating zone methods are capable of producing large single crystals without any crucible interaction but can be challenging with some hexaboride compounds that display incongruent melting. Fig. 6 [10] depicts the La-B phase diagram along with a schematic of a typical floating zone setup [10,11,15,76–84]. Other examples of solid state reactions include mechanochemical synthesis, which relies on the energy produced by collisions between precursor particles and milling media instead of external energy [85], as well as reactive sintering, which is a one-step synthesis and consolidation process [86] to produce LaₓGd₁₋ₓB₆ by combining lanthanum and gadolinium hydrides with boron and then heating the mixture by spark plasma sintering (SPS).

3.2. Melt electrolysis and flux

Melt electrolysis and flux techniques are used to grow crystals within a molten bath, with the main difference between the two being the application of a current (electrolysis). Electrolysis, or electrochemical synthesis, most often utilizes a bath of molten salts [50,87–92] to dissolve the metal and boron pre-
of producing high purity MB₆ single crystals, often several millimeters in length. Due to the metallic character of the bonds in refractory borides, suitable high-temperature solvents are in practice limited to metals [98]. Although no metal has been found to perfectly meet all the requirements, molten aluminum and germanium offer the best compromise and the reducing power of aluminum has proven itself over time, thus remaining the most popular solvent choice. While this technique has been used often to produce crystals of near-perfect stoichiometry, recent studies have shown that the stoichiometry actually varies along the length of the crystal, but only by small amounts (ΔB/M 0.3). Fig. 7 illustrates scanning electron micrographs of (La-Ce)B₆ [Fig. 7(a)] and LaB₆ [Fig. 7(b)] crystals with corresponding plots containing the B/(La + Ce) [Fig. 7(c)] and B/La [Fig. 7(d)] ratios along the lengths of the crystals [48]. A typical experimental set-up involves the heating of high-purity aluminum ingots with the desired precursors in an alumina or aluminum nitride crucible under flowing argon to around 1673 K, followed by a slow cool to room temperature. The MB₆ crystals are then removed by dissolving the aluminum matrix in either HCl or NaOH. Although the crystals are often very high purity, impurities may take the form of aluminum inclusions [48] (as low as 0.02 wt.%) or iron [10,96,101,102] (0.03 wt.% as a result of matrix removal), with the former being easy to locate and avoid.

3.3. Vapor deposition and metal-gas reactions

Vapor deposition and metal-gas reactions are commonly used to produce nano-structured materials and their application in hexaborides includes the synthesis of nanowires [5,103–111], nanobars [112] and nanoobelisks [113]. Chemical vapor deposition (CVD) of hexaboride materials often involves a metal precursor (MₓClₓ, MₓOₓ) heated under the flow of boranes (BₓHᵧ, BₓHₓCe, BₓHᵧ), which grows crystals on an upstream wafer. This process is sometimes accompanied by a catalyst such as nickel [5,103,105,111], especially when metal oxide precursors are used. CVD reactions for hexaborides typically occur at temperatures between 1073 and 1273 K. Zhang et al. [114,115] grew LaB₆ nanowires ranging in diameter from 15 nm to more than 100 nm terminating with [001] surfaces that displayed a high emission current density of 5 × 10⁶ A·cm⁻². Fig. 8 illustrates scanning electron micrographs of LaB₆ nanoobelisks [113] grown using lanthanum chloride and decaborane. In similar fashion to the 1D hexaboride structures produced by CVD using metal oxides or metal chlorides with borane gas, a reaction of pure metal and boron trichloride gas can produce hexaboride nanowires with and without the use of a catalyst. Flowing boron trichloride and hydrogen gas over metal precursors results in the formation of hexaborides and hydrochloric acid. Reaction temperatures for the synthesis of hexaborides typically range between 1273 and 1423 K.

Unlike CVD, physical vapor deposition (PVD) of hexaboride compounds is based on non-reactive techniques [116–121]. This can be accomplished by magnetron sputtering [116], arc evaporation [117], electron beam evaporation [120], and triode sputtering [121] for the deposition of hexaboride coatings. As these types of non-reactive processes involve the vaporization of a hexaboride target, instead of metal and boron precursors, they may be considered as more material rearrangement than

![Fig. 6](image-url) - (a) Phase diagram of the La-B system and (b) the traveling solvent floating zone method by which high-quality crystals, free of boundaries, can be prepared [10].

cursors, although other options such as molten borates [93] can be used. The electrolytically dissolved metal and boron ions within the melt deposit on the cathode and crystallize into MB₆ compounds. The materials used for the cathode (rod) and anode (crucible) vary based on the salts and targeted metal cations, but popular choices include tungsten or molybdenum cathodes and graphite or glassy carbon crucibles. Current densities range from 0.2 to 2 A/cm² and synthesis temperatures are usually around 1273 K. Melt electrolysis produces polycrystalline coatings on the cathode surface and some results indicate increasing grain size with increasing current density [87]. The aluminum flux [8,9,19,37,47,48,81,94–100], a specific form of the solution-melt method, has the distinct advantage
material synthesis. Nevertheless, PVD is capable of producing thin films and coatings of hexaboride compounds. Thermal plasma reactors can also be used to evaporate solid precursors and cause the nucleation of desired compounds from supersaturation of the vapor phase. Szépölgyi et al. [122] injected lanthanum oxide and amorphous boron through a radio-frequency inductively coupled plasma flame, resulting in precursor vaporization and nucleation followed by water cooling to produce agglomerates of spherical LaB₆ particles 10 to 50 nm in size.

3.4. Combustion synthesis

Combustion and self-propagating synthesis techniques represent a broad range of reactions all involving the ignition of materials to drive the formation of oxide and hexaboride compounds [123–132]. Amalajyothia and Berchmans [133] combusted a mixture of metal nitrates, lithium tetraborate and citric acid under argon at 873 K to produce CeB₆ powders with a crystallite size of 200 nm. Dou et al. [134,135] produced LaB₆ and CeB₆ powders through the combustion of metal oxides and boron oxide with magnesium powder as an ignition source. In a similar fashion, Huang et al. [136] combusted calcium hexaborate at 973 K using magnesium powders as an ignition source and reducing agent to produce calcium hexaboride powder. Kanakala et al. [137,138] used a solution of metal nitrates, amorphous boron and carbohydrazide to produce lanthanum, samarium and europium hexaboride powders with a particle size of 500 nm. The authors also noted that while it was possible to produce yttrium and ytterbium hexaboride using the same combustion method, the powders contained a significant fraction of metal borate phases. Selvan et al. [139] developed the reaction under autogenic pressure at elevated temperatures and combusted metal acetates and sodium borohydride (NaBH₄) in a nitrogen environment within a closed stainless steel cell to produce rare-earth hexaboride powders (RB₆, where R = La, Ce, Nd, Sm, Eu and Gd) with a particle size of 200 nm to 10 μm. As with solid-state reactions, combustion synthesis is proven to be more effective when the precursors are well-mixed. Inadequate mixing may lead to incomplete reactions (excess boron or metal oxides) or phase segregation in the case of mixed-metal hexaboride compounds [51]. Well-mixed precursor solutions are capable of producing sub-micron sized hexaboride particles with cubic particle morphologies (Fig. 9).

4. Densification processes

As is typical of covalently-bonded materials, hexaborides can be difficult to sinter into dense compacts. High-pressure/temperature methods such as hot pressing and spark plasma sintering (SPS) are the most common methods used to consolidate hexaboride powders. One method that can be used to track hexaboride sintering events during spark plasma sintering is by monitoring the ram displacement rate under constant load. Sudden changes in ram displacement will appear as peaks or valleys (depending on definition of ram movement as positive or negative) and signify that densification is occurring. Some materials may even display multiple
sintering events depending on the densification phenomena occurring at various temperatures. Sub-micron CaB\(_6\) and SrB\(_6\) produced by combustion synthesis display an initial sintering event during SPS starting at 1273 K, followed by a second sintering event at 1623 K (Fig. 10). During the first sintering event the particles begin to neck and fuse together, followed by coarsening and full densification during the second sintering event. Monitoring displacement rate can be a useful tool for both hot pressing and SPS to determine the points along the heating profile in which maximum consolidation is occurring.

4.1. Hot pressing

Hot pressing is a traditional technique in which pressure and heat are applied to powder simultaneously and is a proven technique in both research and the commercial sector. As with many other non-oxide materials, hexaborides are hot-pressed in an inert or vacuum environment. Inert gases can

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Fig. 8 – Scanning electron micrographs of LaB\(_6\) nanoobelisks and nanowires synthesized with substrates placed (a) 3 cm, (b) 4 cm, and (c) 5 cm downstream from the LaCl\(_3\) precursors. (d-f) Scanning electron micrographs of the nanostructures in (a)-(c), respectively [113].

Fig. 9 – Scanning electron micrograph of sub-micron SrB\(_6\) particles produced by combustion synthesis.
be helium, argon or nitrogen, although some compounds may form nitrides in the presence of nitrogen. Utilizing a continuous flow of these gases ensures that volatiles are flushed from the system. Hot-pressing under vacuum has the advantage that impurities are more likely to volatilize due to the reduced pressure (such as boron oxide in the case of hexaborides), but an adequate pumping system must be in place to allow effective degassing during the entire heating cycle. Hexaboride compounds consolidate well during hot pressing at temperatures several hundred degrees below $T_M$, and it is feasible to reach >98% theoretical density (TD) using this technique. Feng et al. [140] consolidated SmB$_6$ powders by hot pressing at 2223 K and were able to reach 99.6% relative density with a mean grain size of 4.4 μm. Mechanical characterization of these samples revealed a Vickers’ hardness of 20.1 ± 0.7 GPa, Young’s modulus of 271 GPa by bending, a flexural strength of 253 ± 79 MPa, and a fracture toughness $2.1 ± 0.1$ MPa$\cdot$m$^{1/2}$. Sonber et al. [68,141] sintered LaB$_6$ by hot pressing at 2223 K for 2 h at 35 MPa and were able to reach 99.9% relative density. However, when sintering EuB$_6$ powder at 2023 K, a relative density no higher than 86% was achieved. With the addition of 10% TiSi$_2$, a relative density of 96% was accomplished. The low melting temperature of TiSi$_2$ allowed it to act as a liquid-phase sintering aid in the case of the EuB$_6$ consolidation.

In recent years, SPS has been shown to effectively densify a wide variety of materials at lower temperatures and pressures compared to traditional hot pressing [142-159]. Unlike hot-pressing, the SPS environment will be different for various hexaboride compounds depending on their electrical conductivity. Current in the SPS will be more likely to flow through compounds with metallic behavior such as LaB$_6$ compared to the semi-metallic alkaline-earth hexaborides, and therefore the effects of Joule heating will vary between these compounds. Gürsoy et al. [26] utilized SPS to sinter the mixed-metal systems of (Ca-Sr)B$_6$, (Ca-Ba)B$_6$, and (Sr-Ba)B$_6$ at 100 MPa and temperatures between 1673 K and 2173 K. Bao et al. [6] sintered 50nm CeB$_6$ powder to >99% relative density using SPS at 50 MPa and 1823 K, a temperature that is 350 K lower than traditional hot-pressing, and showed that nanopowders consolidated better and at lower temperatures than coarse-grained powders. Cahill et al. [27] used SPS to consolidate CaB$_6$-SrB$_6$ diffusion couples by first pre-sintering powder to 90% relative density at 1473 K for 3 min under 50 MPa pressure and then fusing two pellets together at a temperature of 1723 K for 5 min under 20 MPa pressure. Fig. 11 depicts an SEM image of a fracture surface from a SrB$_6$ pellet sintered at 50 MPa and 1753 K using sub-micron powders. The specimen reached 98% relative density and many of the grains maintain the cubic morphology of the starting powders even after coarsening.

In addition to pressure-assisted sintering, hexaborides have also been consolidated using pressureless sintering. Agaogullari et al. [74] sintered nanocrystalline SmB$_6$ by cold-pressing powder at 800 MPa followed by pressureless sintering at 1923 K for 5 h under flowing argon. They were able to reach 96.8% relative density with only small amounts of SmBO$_3$ present due to residual oxide from powder handling in air. The same process was also used to sinter nanostructured CeB$_6$.
to 95.2% relative density [73]. Sonber et al. [141] pressureless sintered LaB$_6$ powder at 2223 K for 4 h under vacuum after cold-pressing at 280 MPa but were only able to reach 85.1% relative density compared to 99.9% for powders consolidated by hot pressing. Like many other borides, the high melting temperatures and strong covalent bonding of hexaborides limit mass transport and make it difficult to reach high densities with pressureless sintering.

5. Summary

Hexaborides have shown potential for use in a variety of technical fields due largely in part to their unique electrical, magnetic and physical properties. Many of these properties stem from the crystal structure, which contains a network of strongly-bonded boron atoms surrounding a metal atom. Although all hexaborides share this crystal structure, changing the metal atom can have a substantial effect on a variety of physical properties of the compounds. Hexaborides can be produced by solid-state reactions, electrolysis and flux, vapor deposition or metal-gas reactions, and combustion or self-propagation depending on the desired physical state (i.e., powder or single crystal) and purity. Often, these synthesis processes require extended time at elevated temperatures, but new methodologies show that low-temperature and rapid synthesis of hexaborides is possible. As the interest in the unique properties of hexaborides grows, so does the collective knowledge of the structure, synthesis and processing of these fascinating family of compounds.

Conflict of interest

The authors confirm no conflicts of interest exist in the submission of this manuscript.

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