journal

J. Am. Ceram. Soc., **93** [10] 3136–3141 (2010)
DOI: 10.1111/j.1551-2916.2010.03853.x

Unique Preparation of Hexaboride Nanocubes: A First Example of Boride Formation by Combustion Synthesis

Raghunath Kanakala,*[‡,§] Gabriel Rojas-George,[§] and Olivia A. Graeve*[†,‡]

[‡]Kazuo Inamori School of Engineering, Alfred University, Alfred, New York 14802

[§]Department of Chemical and Metallurgical Engineering, University of Nevada, Reno, Nevada 89557

Nanocubes of LaB_6 and $Sm_{0.8}B_6$ have been synthesized using low-temperature combustion synthesis, a technique that had only been used previously for the preparation of oxides. The hexaboride nanocubes were prepared using lanthanum nitrate or samarium nitrate, carbohydrazide, and boron powders. The furnace temperature for synthesis was kept at 320°C, lower than the typical temperature values used in combustion processes for the preparation of oxides. After synthesis, the nanocubes were characterized using X-ray diffraction, scanning electron microscopy, and X-ray photoelectron spectroscopy. The combustion process was analyzed using differential scanning calorimetry, which shows that the formation of the carbohydrazide and nitrate melts as well as the formation of a complex between metal ions and carbohydrazide are crucial steps for the reaction. The technique results in high-purity powders with a unique cubic morphology, in which the corners of the cubes can be used as point sources for efficient electron emission.

I. Introduction

Boride compounds have proven to be essential for myriad applications such as reinforcing phases in metal–matrix composites[1–3] and armor materials.[4] One particular subgroup in this large class of materials includes the hexaborides, which are being used as additives for wear- and corrosion-resistant engineering components,[5] for decorative and thermionic coatings,[6] and for electron emission sources.[7] Here, we demonstrate the first instance of the preparation of boride materials by an efficient combustion synthesis technique at a temperature of 320°C. Combustion synthesis has been utilized since the 1990s for preparing many types of nanocrystalline oxides, as has been shown in countless studies.[8–12] However, boride materials were thought to be unfeasible by this technique. We have selected two compounds, the hexaborides LaB_6 and $Sm_{0.8}B_6$, as model materials for representing the effectiveness of the process for the preparation of borides. The technique results in high-purity powders with a unique cubic morphology, in which the corners of the cubes can be used as point sources for efficient electron emission.

Significant efforts have been directed toward the preparation of boride materials,[13] which for hexaborides include the molten salt technique,[14] borothermic reduction of oxides at varying pressures,[15–17] aluminothermic reduction using aluminum melts,[18] synthesis in autoclaves,[19,20] and thermal plasmas.[21] However, the synthesis temperatures and processing times are always significant, with the lowest synthesis temperature of 400°C achieved only by using long processing times (~4 h) in an autoclave.[20] Our combustion synthesis process for producing borides has a series of advantages, not the least of which are the low temperatures required for processing. The technique is highly efficient involving fast heating rates, short reaction times of just a few seconds, and no need for a protected inert atmosphere, while at the same time being easily scalable. For this reason, it has been used very effectively for the synthesis of oxides, when it is sometimes referred to as the glycine-nitrate process. In this type of synthesis, an exothermic reaction occurs between metal nitrates and a fuel in an oven, muffle furnace, or hot plate. For clarification, our synthesis process is not a subset of the well-known self-propagating high-temperature synthesis technique,[22] which makes use of self-sustaining solid-state reactions between metal and boron powders for making ceramics such as TiB_2 and ZrB_2, both of which result in very high exothermic heats of reaction. Our technique makes use of nitrate salts and an organic fuel mixed in the form of a slurry, resulting in intimate atomic level mixing upon formation of a melt, as will be described later, thus, permitting the formation of very homogeneous compounds. Thus, our process for making borides is truly unique and with the additional advantage that the reactants are easy to handle and do not require protected atmospheres during synthesis.

II. Experimental Procedures

The reactant chemicals for the synthesis included $La(NO_3)_3 \cdot 6H_2O$ (99.99%; Alfa Aesar, Ward Hill, MA), $Sm(NO_3)_3 \cdot 6H_2O$ (99.99%; Alfa Aesar), $CO(NHNH_2)_2$ (98%; Sigma-Aldrich, St. Louis, MO), and boron powders (Noval Industrial Group, Shandong, China). These compounds were thoroughly hand-mixed using a mortar and pestle in the order of nitrate, carbohydrazide, and boron powders. Once mixed, the reactant chemicals were spread as a thin layer at the bottom of a ceramic crystallization dish. The crystallization dish, along with the precursor materials, was introduced into a muffle furnace at room temperature. The furnace was heated along with the reactant chemicals at a moderate rate of ~30°–35°C per minute until the combustion reaction occurred at ~320°C. A typical reaction consists of 10.625 g of $La(NO_3)_3 \cdot 6H_2O$, 1.592 g of boron, and 0.553 g of carbohydrazide, for the case of LaB_6 synthesis, and 10.326 g of $Sm(NO_3)_3 \cdot 6H_2O$, 1.507 g of boron, and 0.523 g of carbohydrazide, for the case of $Sm_{0.8}B_6$ synthesis. The fuel-to-oxidizer ratio, ϕ, for our reactions was 0.08, which is below the stoichiometric ratio of 0.53, making our mixtures significantly fuel lean. These reactant amounts correspond to stoichiometric quantities for obtaining 5 g of either LaB_6 or $Sm_{0.8}B_6$ after the reaction is completed. The washing process involved a series of steps: (1) cleaning with 80 mL of HCl and 20 mL of H_2O for every 1 g of the powder, and centrifuging at 4000 rpm for 30 min, (2) washing with 100 mL deionized water and centrifuging, (3) cleaning with 50 mL H_2SO_4 and 50 mL H_2O for every 1 g of the powder, followed by centrifuging, (4) washing

---

K. Watari—contributing editor

Manuscript No. 27482. Received January 29, 2010; approved April 8, 2010.

*Member, The American Ceramic Society.

This work was financially supported by grants from the U.S. Army Research Office under contract numbers W911NF-06-1-0226 and W911NF-08-1-0330 with Dr. William Mullins and Dr. David Stepp as project managers, by request of the Defense Advanced Research Projects Agency, with Dr. Leo Christodoulou and Dr. Cindy Daniell as program managers.

[†]Author to whom correspondence should be addressed. e-mail: graeve@alfred.edu

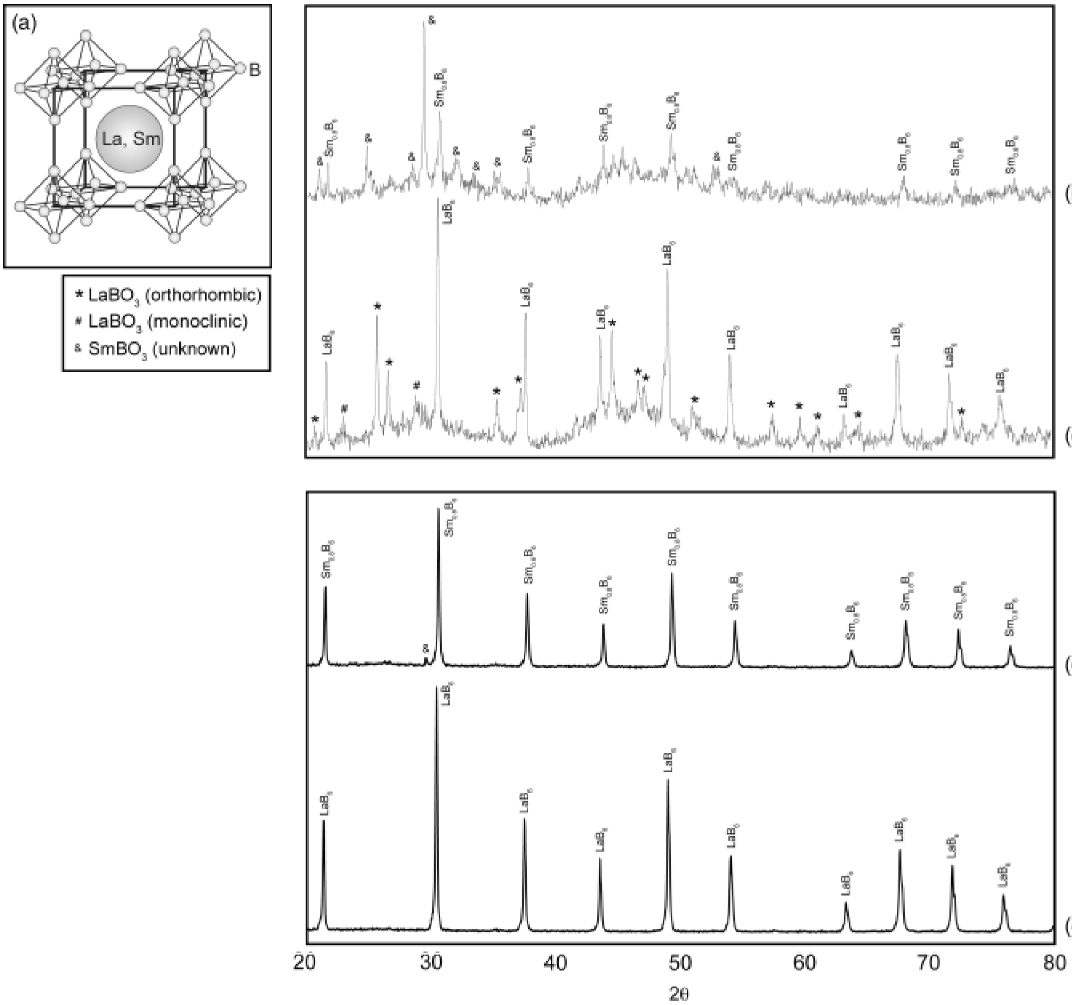


Fig. 1. Crystal structure and X-ray diffraction (XRD) patterns of hexaboride nanocubes. (a) Cubic crystal structure of hexaboride compounds, (b) XRD of as-synthesized powders of $Sm_{0.8}B_6$, (c) XRD of as-synthesized powders of LaB_6, (d) XRD of acid-washed powders of $Sm_{0.8}B_6$, and (e) XRD of acid-washed powders of LaB_6.

with deionized water and centrifuging, and (5) air drying. We used diluted hydrochloric acid (12.1*M*, Fisher Scientific, Pittsburgh, PA) and diluted sulfuric acid (18*M*, Fisher Scientific).

Characterization of the powders was carried out by X-ray diffraction (XRD) using a Philips PW 1800 system (Koningklÿke Phylips Electronics N.V., Eindhoven, the Netherlands), scanning electron microscopy (SEM) using an FEI Quanta 200F system (FEI Company, Hillsboro, OR), X-ray photoelectron spectroscopy (XPS) using a PHI Quantera SXM system (Physical Electronics Inc., Chanhassen, MN), and differential scanning calorimetry (DSC) using a TA Instruments DSC Q10 (TA Instruments, New Castle, DE). XRD measurements were completed using Cu$K\alpha$ radiation without subtraction of the $K\alpha_2$ peak by placing powders on a zero-background holder and slightly tapping them into place to form a smooth surface. The SEM samples were prepared by dispersing the powders in acetone, drop coating the slurry onto a silicon wafer, and sputter-coating with carbon. The XPS measurements were performed using a 200 mm diameter/50 W/15 kV beam. The depth profile for the XPS equipment is ~20 Å. DSC analysis was carried out at a 20°C/min heating rate in alumina cups. The boron powders were also characterized by BET surface area analysis using a Micromeritics (Micromeritics, Norcross, GA) Tristar surface area and porosity analyzer.

III. Results and Discussion

For the synthesis of the LaB_6 and $Sm_{0.8}B_6$, lanthanum nitrate or samarium nitrate and boron powders were mixed with carbohydrazide fuel resulting in an exothermic reaction, according to the following chemical reaction:

$$\mathrm{Ln(NO_3)_3} + 6\mathrm{B} + X\mathrm{(H_2NNH)_2C} = \mathrm{O} \xrightarrow{\Delta} \mathrm{LnB_6} + x\mathrm{N_2} + y\mathrm{H_2O} + z\mathrm{CO_2} + \text{other gases } \mathrm{Ln} = \mathrm{La\ or\ Sm}$$

Our interest in hexaboride materials stems from their unique crystal structure (Fig. 1(a)). The lattice is simple cubic and consists of boron octahedra at each corner of the cube bonded at the apexes. The octahedra have a coordination number of six and consist of the boron atoms, with four adjacent neighbors in every octahedron for every boron atom, and one on the main axis of the cube. The valence electrons of boron are distributed over five bonds. The metal atom is located in the middle of the unit cell with no bonds to the boron atoms. Thus, the metal atoms provide free electrons imparting a metallic character to most of these materials, although some are known to be semiconductors. This, together with the strong bonds between the boron atoms in the framework, produces a series of compounds that have high thermal and chemical stabilities, and low work functions for electron emission applications.

Figures 1(b)–(e) illustrates the XRD patterns for our as-synthesized and washed LaB_6 [PDF #00-0340427] and $Sm_{0.8}B_6$ [PDF #00-056-1206] powders. [Correction added after online publication June 9, 2010: corrected first PDF # in preceding sentence.] From Figs. 1(b) and (c), we can confirm the presence of the desired hexaboride powders. Both sets of powders also contain borate phases of $LaBO_3$ or $SmBO_3$, as noted on the diffraction pattern. Also, a small amorphous hump is observed

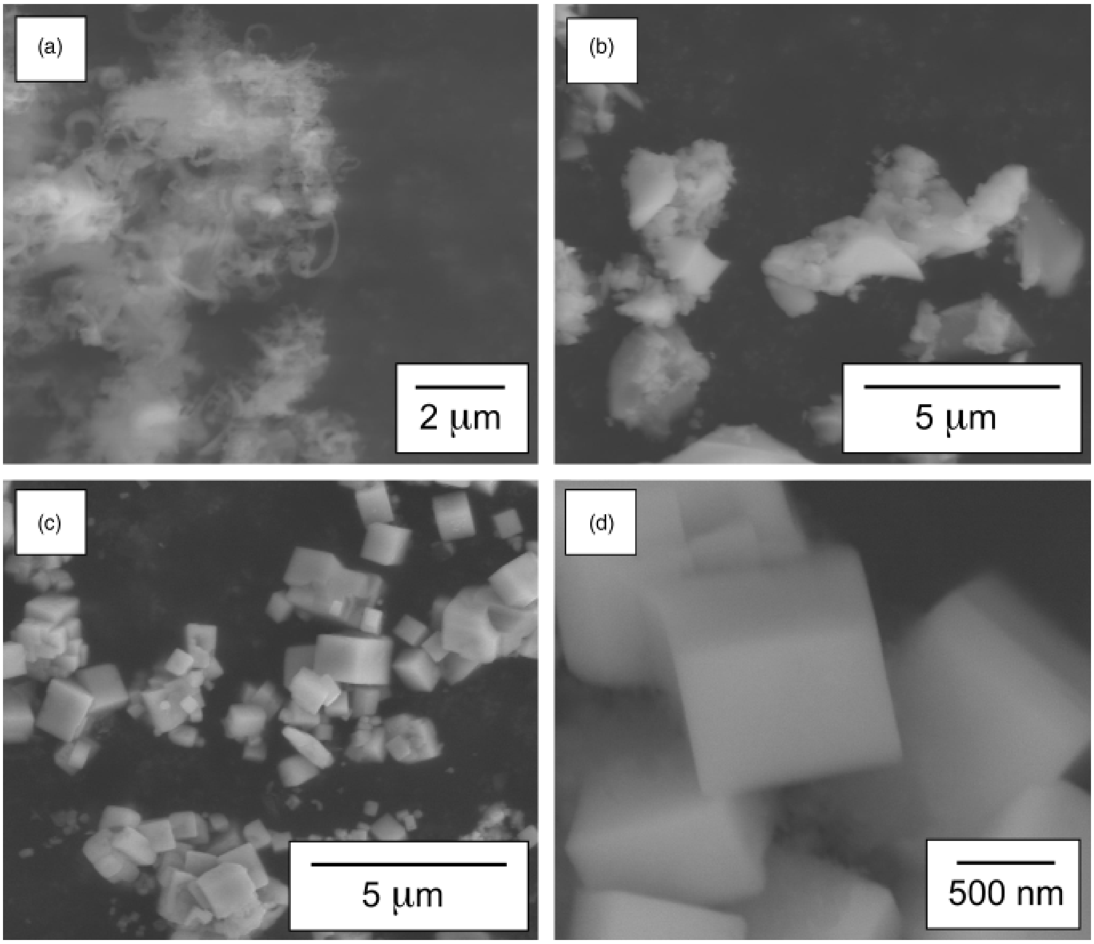


Fig. 2. Scanning electron microscopy of (a) rhombohedral boron powders, (b) as-synthesized LaB_6 powders, and (c, d) acid-washed LaB_6 powders.

between ∼40° and 55° and is characteristic of the as-received boron powders, of which there are some that are left unreacted after synthesis. Compound stability between La, B, and O, can result in an orthorhombic phase [PDF #00-012-0762] at lower temperatures, and a monoclinic phase at temperatures greater than approximately 1500°C [PDF #01-073-1149 or PDF #00-013-0571]. For the case of Sm, B, and O, a hexagonal phase [PDF #00-013-0479] is stable at lower temperatures, and a low-symmetry phase [PDF #00-013-0489], of unknown structure, at higher temperatures.[23] During the synthesis of the LaB_6 phase, we obtain powders that contain a mixture of LaB_6, orthorhombic $LaBO_3$, and monoclinic $LaBO_3$ (minor phase). The orthorhombic $LaBO_3$ phase is predominant over the monoclinic $LaBO_3$ phase because, even if the flame temperature during synthesis is high (typical combustion synthesis reactions exceed 1000°C), the reactants are at the higher temperatures only for a very short time. During synthesis of the $Sm_{0.8}B_6$ phase, we obtain powders with a mixture of $Sm_{0.8}B_6$ and the high-temperature $SmBO_3$ phase. The formation of the high-temperature phase of $SmBO_3$, instead of the hexagonal form, is not clear at this point.

Borates are soluble in hydrochloric acid, whereas hexaborides only dissolve in concentrated sulfuric and/or nitric acid.[24,25] Thus, the as-synthesized powders can be cleaned with hydro-

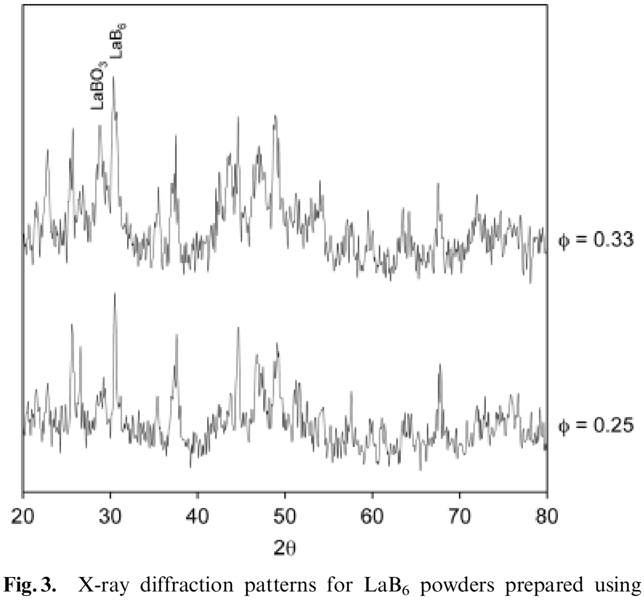


Fig. 3. X-ray diffraction patterns for LaB_6 powders prepared using higher fuel-to-oxidizer, φ, ratios of 0.25 and 0.33. Note that these φ values are still below the stoichiometric φ value of 0.52.

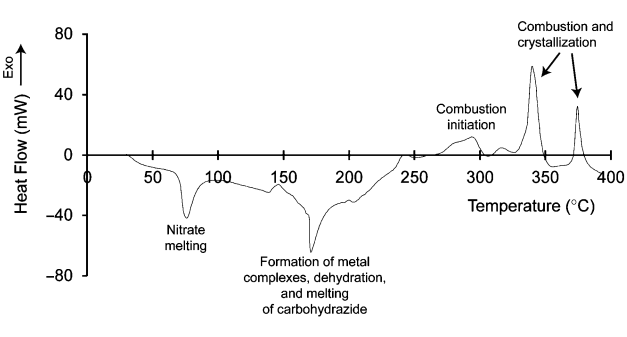


Fig. 4. Differential scanning calorimetry of the combustion reaction between lanthanum nitrate, boron, and carbohydrazide.

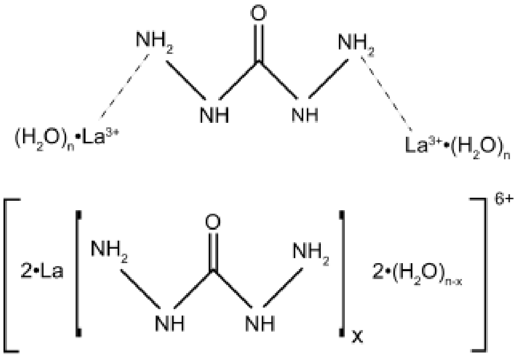
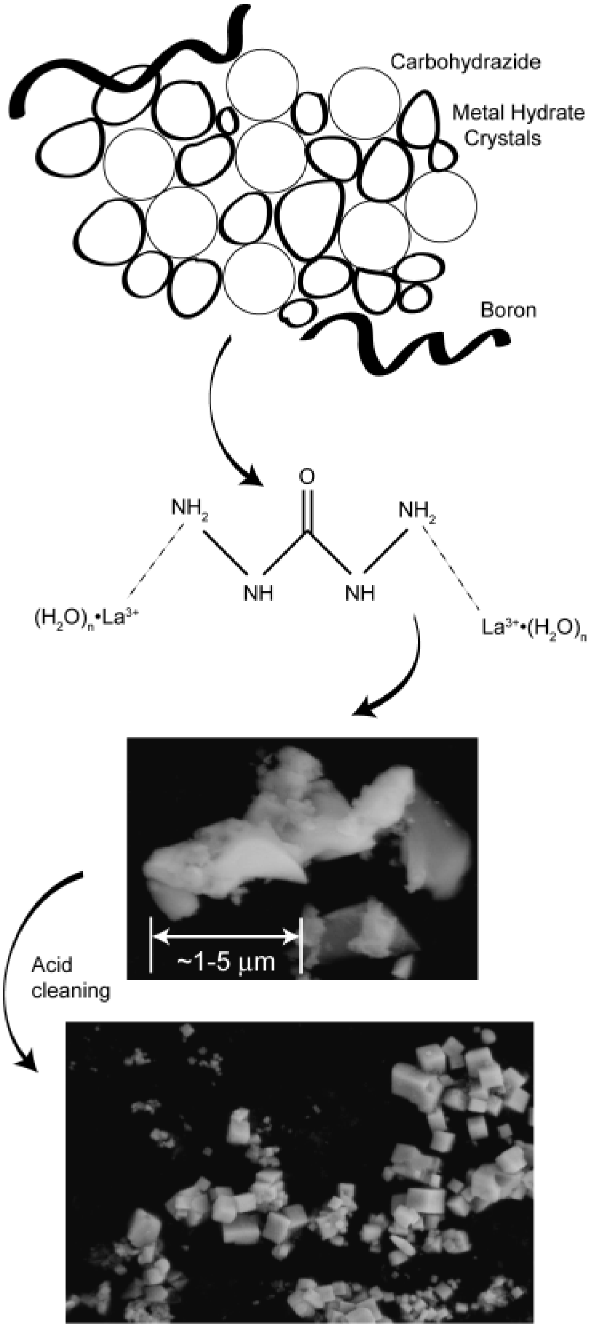


Fig. 5. Two different representations of the carbohydrazide/metal complex, which forms during heating of the reactants at a temperature of approximately 150°–200°C.

chloric acid in order to remove the small amount of borate impurities and then in diluted sulfuric acid to remove the unreacted boron and obtain cuboids of single crystals with cube size dimensions around 500 nm, as illustrated in Figs. 2(c) and (d). Hexaborides slowly decompose in sulfuric acid[26]; thus, some loss of surface material occurs during exposure to sulfuric acid, with the outcome that only the stable cubic morphology is retained, with the faces corresponding to the lower energy {100} surfaces.[27] Once the acid washes are complete, the LaB_6 powders are free of impurity phases (Fig. 1(e)), while the $Sm_{0.8}B_6$ powders exhibit only an extremely small residue of $SmBO_3$ (Fig. 1(d)). The powder yield is about 10%. We are currently working on increasing the yield by improving the cleaning process, so as not to loss as much powder during the acid washing steps.

The synthesis of the hexaborides was accomplished using significantly fuel-lean ($\phi = 0.08$) mixtures, which are close to



Step 1. Physical mixing of the powders. During this process, the metal hydrate crystals come into contact with the carbohydrazide. The boron is added afterwards.

Step 2. Between ~50 and 250°C, melting of the nitrate salts occurs, which results in the formation of a water/nitrate slurry. The molten carbohydrazide and metal ions then form a complex.

Step 3. The combustion reaction begins at around 270°C. After synthesis, the powders contain the hexaboride compound predominantly, and some amount of borate and boron.

Step 4. After removal of impurities with hydrochloric and sulfuric acids, the powders exhibit a cubic morphology, with surfaces corresponding to the low-energy {100} planes.

Fig. 6. Proposed mechanism for the preparation of hexaborides using the combustion synthesis process.

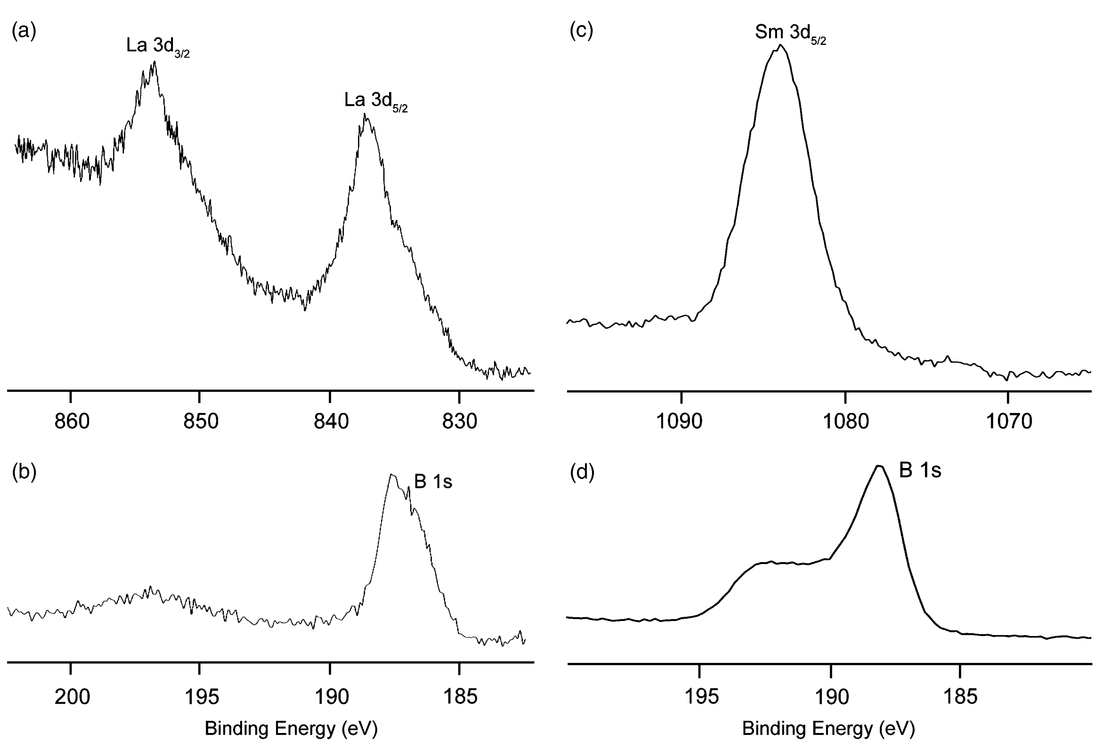


Fig. 7. X-ray photoelectron spectroscopy of (a) La 3*d* signal in LaB_6, (b) B 1*s* signal in LaB_6, (c) Sm 3*d* signal in $Sm_{0.8}B_6$, and (d) Sm 1*s* signal in $Sm_{0.8}B_6$.

seven times lower than the stoichiometric fuel-to-oxidizer ratio of 0.52. As ϕ is increased from 0.08 to 0.25 and 0.33 (Fig. 3) for the case of LaB_6 synthesis, the peaks corresponding to $LaBO_3$ become much more significant, compared with the $LaBO_3$ peaks found for the samples prepared using $\phi = 0.08$ (Fig. 1(c)). Further increasing ϕ to the stoichiometric value results in the expected oxide material (i.e., La_2O_3), as is typically seen in combustion synthesis reactions (not shown). Thus, we confirm that the heat of reaction must be kept as low as possible in order to promote the formation of the borides. The morphologies of the powders at different stages of the process are illustrated in Fig. 2. Figure 2(a) corresponds to the as-received rhombohedral boron powders. The boron powders have a fibrous morphology with a surface area of 17.12 ± 0.08 m^2/g, which we determined from surface area analysis. The as-synthesized powders (Fig. 2(b)) containing the unreacted boron, borate, and hexaboride phases are large, with particle sizes between 1 and 5 μm. After acid cleaning, the cubic morphology is evident (Figs. 2(c) and (d)).

In a conventional combustion synthesis reaction, the reactants are placed in a preheated muffle furnace at temperatures ~500°C; thus, the heating rate is extremely high and results in a reaction within a couple of minutes, depending on the amount of water that needs to be evaporated, because the reaction does not begin until all the water is removed from the system. In our case, if the experiment is completed using the above procedure, we obtain La_2O_3 and borates, with no evidence of hexaborides. However, if the heating of the reactants is attempted at a maximum furnace temperature of 320°C, the reaction results in the desired hexaboride compounds. This mechanism can be explained from DSC analysis (Fig. 4). During heating, a series of both endothermic and exothermic peaks are observed. First, an endothermic peak is observed at 76°C due to melting of the nitrates,[28] followed by a significant endothermic peak at 170°C due to melting of the carbohydrazide,[28] the formation of a complex between carbohydrazide and metal ions,[29] and dehydration. The carbohydrazide has two amine groups (one on each end of the molecule) and can form a complex with La^{3+} ions, as illustrated in Fig. 5. If this mechanism describes our process accurately, then the combustion process can probably occur at a furnace temperature than is lower than what we used. However, we did not test for this because of the large errors associated with temperature measurements in our large muffle furnace, which has errors as high as ±50°C. Subsequent exothermic peaks represent the combustion and crystallization processes. The significant exothermic peaks observed at 339° and 379°C are due to completion of the combustion. All of these steps need to be completed in turn and with enough time for the hexaboride formation to become favorable. If the heating rate is too high, then the final combustion reaction occurs faster than what is required for melting and full mixing of the reactants. Also, the mixing of the reactant powders in the mortar and pestle has to be accomplished in a specific order. If the boron powders are mixed with the nitrates before adding the fuel, the boron covers the nitrate salts, preventing direct contact between the nitrate oxidizer and the carbohydrazide and impeding the reaction. However, if the powders are mixed in the correct order: nitrate and fuel first, then boron, the reaction proceeds successfully. Our proposed mechanism is illustrated fully in Fig. 6.

To determine surface species on the powders, we have used XPS. The representative spectra for LaB_6 (Figs. 7(a) and (b)) illustrates the XPS signal of La 3*d* at 837.9 (La $3d_{5/2}$) and 854.5 (La $3d_{3/2}$), and the B 1*s* peak at 188.2 eV, in agreement with the data obtained in earlier reports[19,20,30] for lanthanum and boron bonding in LaB_6. Based on the scaling of the peak area, the atomic ratio of La to B is 1 to 5.96, which confirms the chemical stoichiometry of LaB_6. Small amounts of nitrogen, oxygen, and carbon, are also detected and are likely due to the adsorption of nitrogen, oxygen, and carbon dioxide gases, on the surfaces of the powders. The signal for lanthanum and boron is very strong, which implies that the oxygen signal is from the very top surface layer, and if there is an oxide coating, it is thin enough that it does not interfere with the electrons from the underlying ions to emerge unaltered. The representative spectra for $Sm_{0.8}B_6$ (Figs. 7(c) and (d)) illustrate the XPS signal of Sm 3*d* at ~1084 eV and the B 1*s* peak at 188 eV for boride bonding in SmB_6. The peak(s) at ~193 eV can be possibly evaluated as B–O.

In summary, a low-temperature combustion synthesis methodology for the synthesis of nonoxide ceramics has been developed. Combustion synthesis is a technique that has been extremely successful for the preparation of oxides, but until now had never been shown to be effective for borides. Current work in our laboratory making use of this process focuses on the preparation of hexaborides such as EuB_6, YbB_6, and YB_6, as well as some diborides.

IV. Conclusions

The present work demonstrates for the first time the preparation of borides materials by combustion synthesis, which until now had only been used for the preparation of oxides. An optimum set of processing parameters for the combustion synthesis of hexaboride materials has been investigated. Our results show that melting of the nitrate and carbohydrazide is crucial for the formation of the borides. At the same time, the fuel-to-oxidizer ratio must be kept low in order to suppress the formation of oxides. Even at the low fuel-to-oxidizer values used in this study, there is a small amount of $LaBO_3$ and $SmBO_3$ that forms during the combustion. Cleaning with hydrochloric acid is successful in removing unwanted borate phases. Subsequent cleaning with sulfuric acid results in the removal of unreacted boron and the formation of a special cubic morphology, for application in electron emission. Thus, with the proper selection of reactants and control of the synthesis conditions, this facile combustion process may be extended for the preparation of a variety of borides, including diborides and dodecaborides.

References

[1] J. A. Christodoulou and H. M. Flower, "The Role of Borides in Near-γ Titanium Aluminides," *Adv. Eng. Mater.*, **2** [10] 631–8 (2000).

[2] K. Morsi and V. V. Patel, "Processing and Properties of Titanium–Titanium Boride (TiB_w) Matrix Composites—A Review," *J. Mater. Sci.*, **42** [6] 2037–47 (2007).

[3] S. C. Tjong and Z. Y. Ma, "Microstructural and Mechanical Characteristics of In Situ Metal Matrix Composites," *Mater. Sci. Eng. R*, **29** [3–4] 49–113 (2000).

[4] W. A. Gooch, B. H. C. Chen, M. S. Burkins, R. Palicka, J. Rubin, and R. Rayichandran, "Development and Ballistic Testing of a Functionally Gradient Ceramic/Metal Applique," *Mater. Sci. Forum*, **308–311**, 614–21 (1999).

[5] X.-H. Zhang, P. Hu, J.-C. Han, L. Xu, and S.-H. Meng, "The Addition of Lanthanum Hexaboride to Zirconium Diboride for Improved Oxidation Resistance," *Scr. Mater.*, **57** [11] 1036–9 (2007).

[6] C. Mitterer, "Borides in Thin Film Technology," *J. Solid State Chem.*, **133** [1] 279–91 (1997).

[7] A. Taran, D. Voronovich, S. Plankovskyy, V. Paderno, and V. Filipov, "Review of LaB_6, Re–W Dispenser, and $BaHfO_3$–W Cathode Development," *IEEE Trans. Electron Devices*, **56** [5] 812–7 (2009).

[8] L. E. Shea, J. M. McKittrick, O. A. Lopez, and E. Sluzky, "Synthesis of Red-Emitting, Small Particle Size Oxide Phosphors Using an Optimized Combustion Process," *J. Am. Ceram. Soc.*, **79** [12] 3257–65 (1996).

[9] O. A. Lopez, J. M. McKittrick, and L. E. Shea, "Fluorescence Properties of Polycrystalline Tm^{3+} Activated $Y_3Al_5O_{12}$ and Tm^{3+}–Li^+ Co-Activated $Y_3Al_5O_{12}$ in the Visible and Near IR Ranges," *J. Lumin.*, **71** [1] 1–11 (1997).

[10] O. A. Graeve, S. Varma, G. Rojas-George, D. Brown, and E. A. Lopez, "Synthesis and Characterization of Luminescent Yttrium Oxide Doped with Tm and Yb," *J. Am. Ceram. Soc.*, **89** [3] 926–31 (2006).

[11] K. Sinha, B. Pearson, S. R. Casolco, J. E. Garay, and O. A. Graeve, "Synthesis and Consolidation of $BaAl_2Si_2O_8$:Eu. Development of an Integrated Process for Luminescent Smart Ceramic Materials," *J. Am. Ceram. Soc.*, **92** [11] 2504–11 (2009).

[12] O. A. Graeve, R. Kanakala, A. Madadi, B. C. Williams, and K. C. Glass, "Luminescence Variations in Hydroxyapatites Doped with Eu^{2+} and Eu^{3+} Ions," *Biomaterials*, **31** [15] 4259–67 (2010).

[13] R. W. Chorley and P. W. Lednor, "Synthetic Routes to High Surface Area Non-Oxide Materials," *Adv. Mater.*, **3** [10] 474–85 (1991).

[14] K. Amalajyothi, L. J. Berchmans, S. Angappan, and A. Visuvasam, "Electrosynthesis of Cerium Hexaboride by the Molten Salt Technique," *J. Cryst. Growth*, **310** [14] 3376–9 (2008).

[15] A. Latini, F. Di Pascasio, and D. Gozzi, "A New Synthesis Route to Light Lanthanide Borides: Borothermic Reduction of Oxides Enhanced by Electron Beam Bombardment," *J. Alloys Compd.*, **346** [1–2] 311–3 (2002).

[16] L.-P. Li, G.-S. Li, W.-H. Su, X.-D. Zhao, and X. Liu, "A Mössbauer Study of $La_{1-x}Eu_xB_6$ Compounds Synthesized at High Pressure and Temperature," *Hyperfine Interact.*, **128** [4] 409–15 (2000).

[17] Y. Liu, W. J. Lu, J. N. Qin, and D. Zhang, "A New Route for the Synthesis of NdB_6 Powder from $Nd_2O_3-B_4C$ System," *J. Alloys Compd.*, **431** [1–2] 337–41 (2007).

[18] P. Peshev, "A Thermodynamic Analysis of Lanthanum Hexaboride Crystal Preparation From Aluminum Flux with the Use of Compound Precursors," *J. Solid State Chem.*, **133** [1] 237–42 (1997).

[19] R. K. Selvan, I. Genish, I. Perelshtein, J. M. Calderon Moreno, and A. Gedanken, "Single Step, Low-Temperature Synthesis of Submicron-Sized Rare Earth Hexaborides," *J. Phys. Chem. C*, **112** [6] 1795–802 (2008).

[20] M. Zhang, L. Yuan, X. Wang, H. Fan, X. Wang, X. Wu, H. Wang, and Y. Qian, "A Low-Temperature Route for the Synthesis of Nanocrystalline LaB_6," *J. Solid State Chem.*, **181** [2] 294–7 (2008).

[21] J. Szépvölgyi, I. Mohai, Z. Károly, and L. Gál, "Synthesis of Nanosized Ceramic Powders in a Radiofrequency Thermal Plasma Reactor," *J. Eur. Ceram. Soc.*, **28** [5] 895–9 (2008).

[22] Z. A. Munir and U. Anselmi-Tamburini, "Self-Propagating Exothermic Reactions: The Synthesis of High-Temperature Materials by Combustion," *Mater. Sci. Rep.*, **3** [7–8] 277–365 (1989).

[23] E. M. Levin, R. S. Roth, and J. B. Martin, "Polymorphism of ABO_3 Type Rare Earth Borates," *Am. Mineral.*, **46** [9–10] 1030–55 (1961).

[24] J. M. Lafferty, "Boride Cathodes," *J. Appl. Phys.*, **22** [3] 299–309 (1951).

[25] T. N. Nazarchuk, E. M. Dudnik, Yu. B. Paderno, and E. V. Yukhimenko, "Interaction of Lanthanum and Samarium Hexaborides with Acid in the Area of Homogeneity," *Soviet Powder Metall. Met. Ceram.*, **23** [3] 242–5 (1984).

[26] L. N. Kugai and T. N. Nazarchuk, "Determination of Free Boron in the Hexaborides of the Rare Earth Elements," *Soviet Powder Metall. Met. Ceram.*, **14** [6] 509–11 (1975).

[27] T. Nakano, S. Baba, A. Kobayashi, A. Kinbara, T. Kajiwara, and K. Watanabe, "Structure Modification of Radio Frequency Sputtered LaB_6 Thin Films by Internal Stress," *J. Vacuum Sci. Technol. A*, **9** [3] 547–9 (1991).

[28] D. R. Lide, *CRC Handbook of Chemistry and Physics*, 71st Edition, CRC Press, Boca Raton, 1990.

[29] L. A. Chick, L. R. Pederson, G. D. Maupin, J. L. Bates, L. E. Thomas, and G. J. Exarhos, "Glycine–Nitrate Combustion Synthesis of Oxide Ceramic Powders," *Mater. Lett.*, **10** [1,2] 6–12 (1990).

[30] C. L. Perkins, M. Trenary, T. Tanaka, and S. Otani, "X-Ray Photoelectron Spectroscopy Investigation of the Initial Oxygen Adsorption Sites on the LaB_6(100) Surface," *Surf. Sci.*, **432** [1] L222–8 (1999). □