Preparation of LaB$_6$ Powders via Calciothermic Reduction using Mechanochemistry and Acid Leaching

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Abstract

This study reports a room temperature mechanochemical route for the synthesis of LaB$_6$ powders originated from related metal oxide powders as La$_2$O$_3$ and B$_2$O$_3$. Ca granules and B$_2$O$_3$ powders were respectively used as reducing agent and boron source in the experiments. This study is actually meaningful to create added value by using the native boron source of Turkey for the production of high-technology boron materials. Milling duration as the most important parameter of mechanochemistry was examined to reveal the ideal production conditions. Mechanochemically synthesized powders were subjected to selective HCl leaching in order to eliminate unwanted phases. Thermochromical software of HSC Chemistry™ program was utilized to determine the reaction probability and to estimate the predicted products. Characterization investigations were carried out by X-ray diffractometer (XRD), differential scanning calorimeter (DSC), particle size analyzer (PSA), stereomicroscope (SM), scanning electron microscope (SEM), transmission electron microscope/energy dispersive spectrometer (TEM/EDS) and atomic absorption spectrometer (AAS). Nanosized LaB$_6$ powders were achieved with/without an insignificant amount of Ca$_3$(BO$_3$)$_2$ phase via mechanochemistry in a high-energy ball mill for 3 h and via leaching with 4 M and 6 M HCl. Lastly, the experimental outputs obtained by a calciothermic reduction were compared with those of magnesiothermic reduction.

Keywords: lanthanum hexaboride powders, calciothermic reduction, mechanochemistry, room temperature process, lanthanum oxide, boron oxide

1. Introduction

Materials based on boron compounds have been explored since 1950s because of their superior properties in respect to chemical bonding, crystal structure and phonon and electron conduction. Especially, rare-earth metal hexaborides have numerous useful physical and chemical characteristics which make them important to investigate (Post et al., 1956; Futamoto et al., 1980; Otani and Ishizawa, 1996; Balakrishnan et al., 2004; Selvan et al., 2008; Wang et al., 2010; Ji et al., 2011; Brewer et al., 2011; Aprea et al., 2013).

Lanthanum hexaboride (LaB$_6$) has attracted significant interest in the last 60 years amongst transition metal borides and rare-earth metal borides (Samsonov et al., 1963; Paderno et al., 1979; Xu et al., 2012; Dou et al., 2012). LaB$_6$ is a refractory ceramic material characterized by high melting point, high strength, high chemical and thermal stability, low vapor pressure, low electronic work function, low resistivity, low thermal expansion coefficient, high transmission stability, high current and voltage capability and high neutron absorbability (Gao et al., 2005; Xu et al., 2006; Zhang et al., 2008; Selvan et al., 2008). LaB$_6$ is built from B$_6$ type crystal structure (octahedrons in cubic hexaboride) in which boron sublattice is electron-deficient and requires electron transfer from the metal atoms in order to be stabilized (Swanson and McNeely, 1979; Mitterer et al., 1996). Furthermore, these boron octahedrons are united by very strong covalent bonds giving the crystals their characteristic hardness (Ji et al., 2011). LaB$_6$ is defined as a dense Kondo material which show several interesting phases such as antiferro-quadrupolar ordered phase and antiferromagnetic ordered phase in the effect of magnetic field and temperature (Tanaka et al., 2004; Carlsson et al., 2005; Jha et al., 2012). According to the phase diagram of the La-B system, there is one congruently melting LaB$_6$ compound at 2715 °C, a peritectic LaB$_6$ phase at 1800 °C and an unstable LaB$_6$ phase at ~2007 °C (Massalski et al., 1990; Schlesinger et al., 1999).

All these superior properties make LaB$_6$ suitable to use as components of high-energy optical systems, sensors for high resolution detectors, electrical coatings for resis-
LaB₆, coatings for high-current hot cathodes, thermionic materials and to use in nuclear technology (Balakrishnan et al., 2004; Bao et al., 2011). It can also be used in wear and corrosion resistant hard coatings for decoration of consumer products such as eye-glass frames and wrist-watch casings (Mitterer et al., 1996; Selvan et al., 2008). Single crystalline LaB₆ nanowires are one of the most widely used electron emitter in electron gun, which can offer about 10 to 15 times higher brightness, higher emission stability, lower energy spread and longer service life than the tungsten cathodes utilized in a large variety of devices such as high-resolution electron microscopy, electron beam writing units, vacuum electron beam welding machines, microwave tubes, free electron lasers, X-ray tubes, electron beam surface reforming and electron beam lithography devices (Ahmed et al., 1975; Perkins et al., 1999; Chen et al., 2004; Wen et al., 2004; Zhang et al., 2006, 2007, 2008; Wang et al., 2009; Qin et al., 2010; Bao et al., 2011). Moreover, LaB₆ nanomaterials are candidates to motivate the new designs of nanoscale electronic devices operated at high temperatures with the need of enhanced electron collection and injection properties (Brewer et al., 2011). Also, LaB₆ has exceptional thermoelectric properties at low temperatures providing their usage in solid-state cryocooling, thermoelectric refrigerators, generators and single-photon detectors operating at temperatures near to the boiling point of liquid helium which serve in technical applications including quantum computing, quantum cryptography, homeland security, defect control in microchips, astronomy, chemical analysis and particle physics (Carlsson et al., 2005; Petrosyan et al., 2012; Jha et al., 2012). Recently, LaB₆ nanoparticles have been proved as effective materials in near-infrared absorption enabling application in reduction of solar heat gain (Yuan et al., 2011). Additionally, LaB₆ is considered as a potential grain refining agent in Al alloys due to its role as an effective, stable and reliable nucleation substrate for Al during the solidification process (Li et al., 2012).

Many production techniques have been applied in the preparation of lanthanum hexaboride (Baranovskiy et al., 2007; Loboda et al., 2009). Traditionally, LaB₆ has been synthesized by high temperature reaction processes such as direct solid-phase reaction of the corresponding elements or compounds, carbothermal reaction of the lanthanum oxide and B or boron carbide (BₓC) method (Post et al., 1956). In industry, carbothermal reduction and boron carbide method have been widely used due to their low cost and simple equipment (Dou et al., 2011; Hasan et al., 2013). However, disadvantages in these methods such as high content of carbon or high processing temperature limit the possibility of preparing LaB₆ powders with high purity and small particle sizes (Dou et al., 2012). Moreover, powders prepared by these conventional methods have generally poor sinterability (Dou et al., 2012). Floating zone method and electro synthesis have been also developed conventionally in order to obtain LaB₆ crystals (Verhoeven et al., 1976). Essentially, floating zone method has been carried out to produce single crystals by using laser or RF heating (Otani and Ishizawa, 1996; Otani et al., 2000). Electro synthesis of LaB₆ crystals has been applied by molten salt technique from an electrolyte consisting of La chlorides/oxydes, boron sources (B₂O₃, Li₂B₄O₇ etc.) and chloride/fluoride agents (LiCl, LiF, etc.) (Amalajyothi et al., 2008, 2011). For a number of years, researchers have tried to obtain LaB₆ in different forms such as particles, whiskers, rods or cubes using various fabrication techniques. Recently, nanosized (nanocubes and nanorods) or submicron LaB₆ powders have been obtained by using low temperature synthesis in an autoclave and self-propagating high-temperature synthesis (SHS) methods (Ji et al., 2011; Dou et al., 2012). Autoclave systems provide an alternative route for synthesizing LaB₆ at lower temperatures than used in traditional methods (Wang et al., 2010). SHS methods have high reaction speed, simple equipment and low energy consumption but after ignition, the reaction process becomes uncontrolled which results in the occurrence of intermediate phases in the reaction products (Dou et al., 2011). LaB₆ whiskers, wires, tubes and obelisks in nano- or micro-scales have been produced by chemical vapor deposition technique (CVD) (Motojima et al., 1978; Zhang et al., 2006). CVD methods include self-catalyst or metal-catalyst (Au, Pt, etc.) growth of LaB₆ on a substrate based on the catalytic reaction of La element/compound containing powders and boron (BCl₃, BₓHᵧ etc.), hydrogen and argon containing gas mixtures (Ji et al., 2011).

It is significant to develop an efficient method of preparing technologically important LaB₆ powders in high purity, small particle size and various morphologies. It has been attracting more attentions to find new synthesis strategies with low reaction temperature, easy to handle precursors, simple process control, less equipment requirements and low cost. Compared with the above-mentioned production techniques, mechanochemistry is a novel, simple and room temperature process which enables a great degree of controlling the product microstructure (content, shape, size, etc.) and obtaining highly pure materials (Suryanarayana, 2001). To the best of our knowledge, there is recently one report on the fabrication of LaB₆ powders via magnesiothermic reduction forced by ball milling process (Agaoğullari et al., 2012b; Agaoğullari, 2014).

In this study, LaB₆ powders originated from related metal oxide powders (as La₂O₃ and B₂O₃) were synthesized at room temperature, via calcthoeromic reduction using mechanochemistry. Consequently, this study will contribute the first results of the mechanochemically synthesized LaB₆ powders from La₂O₃-B₂O₃-Ca blends to the archival literature.
2. Experimental procedure

The experimental procedure of this study comprises the identification of raw materials, the step-by-step synthesis of LaB$_6$ powders, the purification treatments conducted on the synthesized powders and the characterization investigations carried out at each stage of the overall process.

2.1 Raw materials

The synthesis of LaB$_6$ was originated from its oxide powders such as La$_2$O$_3$ (ABCRTM, in purity of 99.99 %), B$_2$O$_3$ (ETI Mine, in purity of 98 %) powders were used as a native boron source for the formation of boride phase. Ca (Alfa AesarTM, in purity of 99.5 %) granules were utilized as a reducing agent in order to examine their influence on the production of LaB$_6$. The images of all raw materials were captured by using a ZeissTM Discovery.V12 stereomicroscope (SM) coupled with a Zeiss TM Axiocam ERc5s high resolution digital camera. SM images of the raw materials are represented in Fig. 1(a) through Fig. 1(c). Figs. 1(a) and (b) more or less give an idea about the average particle sizes of La$_2$O$_3$ and B$_2$O$_3$ since their SM images respectively have the magnification scale (25X) of 200 and 500 µm. However, Fig. 1(c) whose magnification scale (8X) is 1000 µm obviously shows the average size of the Ca granules as 3 mm.

The crystalline phases of all raw materials were identified using a BrukerTM D8 Advanced Series X-ray diffractometer (XRD) with CuKα (1.54060 Å) radiation in the 2θ range of 10–90° incremented at a step size of 0.02° at a rate of 2°/min. International Center for Diffraction Data® (ICDD) powder diffraction files were utilized for the crystalline phase identification of the raw materials. The XRD patterns of La$_2$O$_3$, B$_2$O$_3$ and Ca granules are illustrated in Fig. 2(a) through Fig. 2(c), respectively. Each figure shows diffraction peaks belonging only to the pure material with no trace of impurities. Although Fig. 2(a) exhibits intense crystalline peaks belonging to its content, Fig. 2(b) shows the characteristic peak structure of amorphous B$_2$O$_3$. The XRD peaks of Ca given in Fig. 2(c) have low intensities arising from its granule form which was very difficult to grind in an agate mortar applied for the proper analysis in the powder diffractometer.

Particle size measurements were conducted in a MalvernTM Mastersizer 2000 particle analyzer using distilled water as the aqueous media in order to determine the accurate particle sizes of the raw materials having powder forms. Figs. 3(a) and (b) represent the respective particle size distributions of the La$_2$O$_3$ [d(0.1) = 7.5 µm, d(0.5) = 28.8 µm, d(0.9) = 67.9 µm] and B$_2$O$_3$ [d(0.1) = 268.5 µm, d(0.5) = 438.8 µm, d(0.9) = 708.2 µm] powders. As seen in Figs. 3(a) and (b), the average particle sizes of the La$_2$O$_3$ and B$_2$O$_3$ starting powders were measured as 33.6 µm and 466.9 µm, respectively.

Powder blends containing stoichiometric amounts of reactants for synthesizing LaB$_6$ powders were prepared according to the ideal reduction reaction given in Eq. (1).

$$\text{La}_2\text{O}_3 + 6\text{B}_2\text{O}_3 + 21\text{Ca} \rightarrow 2\text{LaB}_6 + 21\text{CaO} \quad (1)$$
For each run, powder batches of 6 g were weighed in a Precisa™ XB320M sensitive balance (precision: 0.001 g). Powder batches contained 1.233 g La₂O₃, 1.581 g B₂O₃ and 3.186 g Ca in regard of the 1.543 g LaB₆ formation reaction in Eq. (1). The prepared powder batches are hereafter referred to as La₂O₃-B₂O₃-Ca powder blends.

### 2.2 Mechanochemical synthesis

The prepared La₂O₃-B₂O₃-Ca powder blends were homogenized in a WAB™ T2C Turbula blender for 1 h prior to mechanochemical synthesis experiments. The homogenized powder blends were mechanochemically synthesized by using a multi-axial and vibratory high-energy ball mill, Spex™ 8000D Mixer/Mill, with a rotation speed of 1200 rpm. Non-milled powders, homogenized but not subjected to mechanochemical synthesis, were hereafter referred to as-blended (ab) powders and were used as references for the comparison with the milled ones.

In the mechanochemical synthesis experiments, ball-to-powder weight ratio (BPR) was chosen as 10:1. The milling container was a hardened steel vial with a capacity of 50 ml and the milling media was 50 pieces hardened steel balls with a diameter of 6 mm. Ar gas (Linde™, in purity of 99.999 %) was preferred as the milling atmosphere. The milling vials were evacuated to about 10⁻² Pa and back filled with Ar gas in a Plaslabs™ glove box to prevent surface oxidation and to prevent contamination of powder particles with oxide and nitride phases arising from the presence of air. After sealing the vials, milling was continually conducted at different durations up to 3 h. Preliminary experiments carried out intermittently and continuously up to a certain milling duration resulted in different products because the complete reaction took place by means of the internal heat generated from the repeated collisions of the reactant particles. The milled powders were unloaded again under Ar atmosphere in the glove-box. They are hereafter referred to as mechanochemically synthesized La₂O₃-B₂O₃-Ca powders.

### 2.3 Selective acid leaching

Mechanochemically synthesized La₂O₃-B₂O₃-Ca powders in which the reduction reaction completed contained LaB₆, CaO, etc. phases together as the intermediate products. Selective HCl (Merck™, in concentration of 37 %) leaching was applied on these products under the effect of ultrasonic stirring and heating using a Bandelin Sonorex™ RK-100 H ultrasonic bath due to the fact that LaB₆ is insoluble in HCl. Leaching treatment enabled the removal of the unwanted phases and also Fe impurity which were worn off from the milling vial and milling balls. 4 M and 6 M HCl were used as the leaching solutions. This means that the intermediate products were leached using excess HCl molarity with the intention of obtaining pure LaB₆ powders. After a series of pre-experiments, leaching parameters such as solid-to-liquid ratio of the leaching solution, leaching duration and leaching temperature were fixed respectively to 1 g/10 cm³, 30 min and 80 °C. During the first few seconds of the leaching treatments, the intermediate products violently reacted with the leaching solutions, arising from the high solubility of CaO in HCl solution as in the reactions given in Eqs. (2)–(4).

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \\
\text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} \\
\text{Ca(OH)}_2 + 2\text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}
\]

At the end of leaching treatment, the solutions containing insoluble solids were subjected to repeated centrifuging in a Hettich™ Rotofix 32A centrifuge with a rotation speed of 3500 rpm for 30 min, repeated decanting and repeated washing with distilled water and lastly remained solids were dried under air in a FN 500 stove at 120 °C for 24 h. Supernatant liquids decanted from the solids after each centrifuging-decanting-washing treatment were collected into a volumetric flask and were equated to 150 ml with distilled water for the subsequent instrumental analysis. After each centrifuging-decanting-washing treatment, a few drop of leaching solution was added into...
Mechanochemically synthesized and leached powders were carried out using excess HCl molarity, the HCl adsorption on the boride powders can be also prevented by this detection method. Moreover, pH measurements were carried out on the supernatant liquids decanted from the solids after the last washing procedure, by using Thermo ScientificTM Orion Star A211 pH meter. The measured pH values varied between 5.5 and 6.5, indicating that there was not residual HCl in the media at the end of the repeated treatments. These findings conformed well to the results of AgCl precipitation method. So, the final products originated from the mechanochemically synthesized and leached La$_2$O$_3$-B$_2$O$_3$-Ca powders.

2.4 Characterization

XRD investigations of the as-blended, mechanochemically synthesized and leached powders were performed in a BrukerTM D8 Advanced Series powder diffractometer and in a PANalyticalTM X’Pert$^\text{R}$ powder diffractometer using the same conditions for the raw materials. As-blended and mechanochemically synthesized powders were imaged by the same stereomicroscope utilized for the raw materials. Particle size measurement was conducted on the leached powders using a MicrotracTM Nano-flex particle size analyzer (PSA) equipped with a Bandelin Sonopuls$^\text{TM}$ ultrasonic homogenizer. Thermal properties of the as-blended and mechanochemically synthesized powders were examined in a TA$^\text{TM}$ Instruments SDT Q600 differential scanning calorimeter (DSC): For each run, 15 mg of powders was placed in an alumina crucible and heated up to 1100 °C at a heating rate of 10 °C/min under Ar atmosphere. After DSC analyses, mechanochemically synthesized and heated powders were subjected to an additional XRD analysis for detecting the obtained phases. Microstructural characterizations and energy dispersive spectroscopy (EDS) analyses of the mechanochemically synthesized and leached powders were carried out using a HitachiTM TM-1000 scanning electron microscope (SEM) operated at 15 kV and also using a Jeol$^\text{TM}$-JEM-2000EX transmission electron microscope (TEM) operated at 160 kV. For SEM analysis, the specimens were prepared by following the procedure of dissolving the powders in C$_2$H$_5$OH (MerckTM, in purity of 99.9%), syringing them onto a base plate, drying them in air and coating their surfaces with a thin layer of gold using a PolaronTM SC7620 Sputter Coater to enhance their conductivities. For TEM analysis, the particles were dispersed in the C$_2$H$_5$OH and a drop of it was taken on a porous carbon film supported on a copper grid and dried in a Jingke$^\text{TM}$ Scientific Instrument vacuum oven. EDS results were reported as the arithmetic mean of three different measurements taken from the same region in the sample. Furthermore, the amounts of elements (B, Ca and Fe) in the supernatant liquid after the purification by leaching process were analyzed in a Perkin ElmerTM 1100B atomic absorption spectrometer (AAS).

3. Results and discussion

HSC Chemistry$^\text{TM}$ Ver. 4.1 program was utilized for the reaction interpretations of the La$_2$O$_3$-B$_2$O$_3$-Ca system. The Gibbs free energy change and the enthalpy change versus temperature curves of the La$_2$O$_3$-B$_2$O$_3$-Ca system up to 2000 °C were graphed by using thermochemical software and they were illustrated in Fig. 4. The reaction has a large negative free energy change between –4100 and –2700 kJ in the temperature range of 0–2000 °C. It means that the reaction in Eq. (1) takes place spontaneously and therefore it is thermodynamically feasible at room temperature and above. Furthermore, a large negative enthalpy change between –4150 and –4510 kJ in the temperature range of 0–2000 °C implies that a large amount of heat is released during the occurrence of the reaction. It can be predicted that the vial temperature will significantly increase during milling due to these exothermic reactions. As seen in Fig. 4, the slope of the enthalpy change-temperature curve varies at some intervals. This is likely due to the melting of B$_2$O$_3$ at 450 °C, the formation of calcium borate phases in different compositions (CaB$_2$O$_4$, CaB$_4$O$_7$, CaB$_6$O$_{10}$, Ca$_2$B$_2$O$_5$, Ca$_2$B$_6$O$_{11}$ and Ca$_3$B$_{12}$O$_{22}$) at 600–1000 °C, the melting of Ca at 840 °C and the boiling of Ca at 1485 °C (Chen et al., 2008; Erfani et al., 2012).

It is already known from our previous study conducted on the La$_2$O$_3$-B$_2$O$_3$-Mg system that its related reaction has a large negative free energy change between –3300 and –1700 kJ and a large enthalpy change between –3440 and –3930 kJ, in the temperature range of 0–2000 °C (Ağaoğulları et al., 2012b). Besides, the slope of the enthalpy change-temperature curve for the La$_2$O$_3$-B$_2$O$_3$-Mg system arises from the melting of B$_2$O$_3$ at 450 °C, the melting of Mg at 650 °C, the formation of magnesium borate phases in different compositions (MgB$_2$O$_4$, Mg$_2$B$_2$O$_7$ and Mg$_3$B$_2$O$_6$) at 700–1000 °C and the boiling of Mg at 1095 °C (Ağaoğulları et al., 2012a; 2012b). On the basis of the enthalpy changes calculated by thermochemical software in case of using Ca or Mg as a reducing agent, it can be stated that calcium borate phases emerged at about 100 °C lower temperatures than those of magnesium borate phases. Furthermore, it is clearly understood that the calciothermic reduction of related oxides is more favorable than their magnesiothermic reduction since their free energy difference at the same temperature is about 800–
1000 kJ. Thus, the use of Ca instead of Mg as a reductant seems to be more suitable in the synthesis of LaB₆ powders according to the thermodynamic calculations. However, the calcium borates regarded as unwanted phases in the boride synthesis form in several compositions at relatively lower temperatures than those of magnesium borates and hence their negative influence on the production step could be considered as a probability. It should be also noted that the results of the thermodynamic calculations show only the equilibrium phase composition at room and elevated temperatures without considering synthesis history and reaction kinetics. Actually, mechanochemical synthesis process is related to the repeated fracturing and repeated welding mechanism. Besides, the contact points between the particles provide favorable conditions for the formation of the products. Due to the fact that mechanochemical synthesis process is far from equilibrium, synthesized phases cannot be expected to have complete consistency with the thermodynamically calculated phases.

Figs. 5(a) through (g) represents the XRD patterns of the as-blended and mechanochemically synthesized La₂O₃-B₂O₃-Ca powders using a 10:1 BPR in a Spex™ 8000D Mixer/Mill up to a milling duration of 3 h.

Since Ca granules had an average size of 3 mm, they were milled for 30 min prior to the homogenization treatment, in the same conditions (BPR, media, atmosphere and container of milling, type and speed of mill, etc.) with those of mechanochemical synthesis experiments in order to obtain reduction in their sizes. According to Fig. 5(a), as-blended powders contain La₂O₃ (ICDD Card No: 71-5408, Bravais lattice: primitive hexagonal, a = b = 0.393 nm, c = 0.614 nm), B₂O₃ (ICDD Card No: 76-1655, Bravais lattice: primitive hexagonal, a = b = 0.433 nm, c = 0.839 nm) and Ca(OH)₂ (ICDD Card No: 72-0156, Bravais lattice: primitive hexagonal, a = b = 0.358 nm, c = 0.489 nm) phases. Although B₂O₃ has a large characteristic amorphous peak in the 2θ range of 15–40° (Fig. 2(b)), it can be seen very slightly at the same range in the XRD pattern of the as-blended powders (Fig. 5(a)) with the peaks of other phases. It is well known that Ca powders easily absorb humidity and form calcium hydroxide at room temperature. Milled Ca powders reacted with humidity during handling in the laboratory atmosphere and hence Ca(OH)₂ phase was observed instead of Ca in the XRD pattern of the as-blended powders. As seen in Figs. 5(b), (c) and (d), mechanochemically synthesized La₂O₃-B₂O₃-Ca powders for 30 min, 45 min and 1 h durations have La₂O₃ and Ca(OH)₂ phases, indicating that there is still no reaction between the contacting particles. However, the intensities of these phases decrease as milling duration increases from 30 min to 1 h. This designates a gradual decrease in their crystallite sizes and an increase in their lattice deformations, which means that the reaction is getting closer step by step. Unlike Fig. 5(a), no slight peaks belonging to the B₂O₃ phase can be detected in the XRD patterns of the 30 min, 45 min and 1 h milled powders (Figs. 5(a)–(c)), whose absence is attributed to its further amorphization during mechanochemical synthesis. Besides, there are very small incubations of LaB₆ (ICDD Card No: 34-0427, Bravais lattice: primitive cubic, a = b = c = 0.416 nm) and CaO (ICDD Card No: 70-5490, Bravais lattice: face-centered cubic, a = b = c = 0.482 nm) phases at about 37.5° at the end of 1 h milling (Fig. 5(d)). Further 30 min milling (Fig. 5(e)) results in LaB₆, CaO and Ca₃(BO₃)₂ (ICDD Card No: 70-0868, Bravais lattice: primitive rhombohedral, a = b = 0.864 nm, c = 1.185 nm)
phases in addition to very small amounts of unreacted La2O3 and Ca(OH)2. X-ray reflections for the LaB6 phase comprised eight peaks at values of 21.354°, 30.387°, 37.445°, 43.517°, 48.969°, 53.995°, 67.564° and 71.757° which are respectively indexed as (100), (110), (111), (200), (210), (211), (300) and (310) family of planes. After milling for 2 h, La2O3 and Ca(OH)2 phases disappear and the composition of the mechanochemically synthesized powders includes only LaB6, CaO and Ca3(BO3)2 phases (Fig. 5(f)). The formation mechanism of Ca3(BO3)2 phase can be explained with the reaction of B2O3 and CaO particles in regard of Eq. (5). However, the emergence of Ca3(BO3)2 phase is unexpected considering the theoretical products of the ideal reduction reaction given in Eq. (1).

$$3\text{CaO} + 2\text{B}_2\text{O}_3 \rightarrow \text{Ca}_3(\text{BO}_3)_2$$

(5)

As compared with the mechanochemical synthesis of La2O3-B2O3-Mg powder blends using the same milling conditions, it is obvious that calciothermic reduction provides a complete reaction 45 min earlier than that of magnesiothermic one in which LaB6 and MgO phases occurred after milling for 2 h 45 min (Ağaoğulları et al., 2012b). Dissimilar to the magnesiothermic reduction of La2O3 and B2O3 powder blends, milled products of the calciothermic reduction contain a borate compound of the reducing agent since Ca is more favorable to form borate phase than Mg. Fig. 5(g) does not show any difference in the phase types of the 3 h milled powders in comparison with Fig. 5(f) because LaB6, CaO and Ca3(BO3)2 are still in the microstructure. However, there is a remarkable increase in the intensities of LaB6 and CaO phases. On the basis of this intensity increment, extended milling durations up to 5 h were conducted on the La2O3-B2O3-Ca powder blends: Broadening of the LaB6 and CaO peaks were observed instead of further intensity increment. It means that prolonged milling time does not contribute to the chemical reaction anymore after 3 h, but it contributes to the size reduction of the particles. Additionally, it should be stated that the actual mechanochemical reaction is different than the ideal reduction reaction in Eq. (1). So, the actual mechanochemical reaction in equilibrium amounts can be indicated as in Eq. (6) on the basis of the experimental results in Fig. 5.

$$\text{La}_2\text{O}_3 + 7\text{B}_2\text{O}_3 + 21\text{Ca} \rightarrow 2\text{LaB}_6 + 18\text{CaO} + \text{Ca}_3(\text{BO}_3)_2$$

(6)

The ideal reduction reaction in Eq. (1) includes 6 moles of B2O3 whereas 7 moles of B2O3 is present in the actual reaction to represent the formation of Ca3(BO3)2 phase. Due to the fact that the initial powder blends were prepared in regard of ideal reaction in Eq. (1) without considering the occurrence of borate phase, it should be also mentioned that the obtained LaB6 phase can include an amount of sub-boride phases such as La0.983B6 (ICDD Card No: 70-8265, Bravais lattice: primitive cubic, a = b = c = 0.41561 nm), LaB5.83 (ICDD Card No: 78-2381, Bravais lattice: primitive cubic, a = b = c = 0.41564 nm), LaB5.892 (ICDD Card No: 75-1414, Bravais lattice: primitive cubic, a = b = c = 0.41569 nm) and LaB5.892 (ICDD Card No: 75-1415, Bravais lattice: primitive cubic, a = b = c = 0.41571 nm). The possibility of containing a sub-boride phase such as LaB6-x is higher than that of La1-xB6. Because an amount of Ca3(BO3)2 emergence and 1 mole lack of B2O3 according to the reaction in Eq. (5) could decrease the number of boron atoms for the boride formation. Although the use of Ca as a reduc tant provided shorter reaction duration than that of Mg, it could change the composition and hence the quality of the boride products, considering the formation probability of sub-borides.

Figs. 6(a) through (g) shows the SM images of the as-blended and mechanochemically synthesized La2O3-B2O3-Ca powders, for different durations up to 3 h. SM images can be helpful to control the reaction proceeding from the general appearance of the powders. The difference between as-blended and milled powders is clearly seen from Figs. 6(a)–(g). As-blended powders contain white La2O3, B2O3 and Ca(OH)2 clusters in the microstructure (Fig. 6(a)). After 30 min milling, white powders turned to gray with an indication of cluster disappearance and size reduction (Fig. 6(b)). The microstructures of the 30 min, 45 min and 1 h milled powders are very similar (Figs. 6(b)–(d)) in accordance with the XRD patterns in Figs. 5(b)–(d) exhibiting the same phases. The blurred SM images in Figs. 6(b)–(d) seem as Ca(OH)2 having the highest weight ratio in the overall powder blend (~53 %) covered the La2O3 and B2O3 particles during milling process. As compatible with the XRD pattern in Fig. 5(e), the microstructure changed after 1.5 h milling (Fig. 6(e)) in which the reaction took place but unreacted La2O3 and Ca(OH)2 are still present. As the reaction completely took place at the 2 h milling duration without leaving unreacted La2O3 and Ca(OH)2 behind (Fig. 5(f)), the color of the powders turned to dark and its morphology changes to a more stable agglomerated form (Fig. 6(f)) in which small LaB6 particles are embedded in CaO and Ca3(BO3)2.

The SM images in Figs. 6(f) and (g) are almost the same with each other since they only have LaB6, CaO and Ca3(BO3)2 phases after the complete reaction obtained at 2 h and after extended milling up to 3 h. It should be noted that the kinetics or the overall rate of the mechanochemical synthesis process depends on the kinetics of the milling in which newly fractured surfaces become active for the reaction initiated by the reducing agent. Mean-
while, fresh surfaces of the particles have tendencies to agglomerate with each other. This phenomenon results in a morphological difference between Figs. 6(b)–(d) and Figs. 6(e)–(g).

The DSC thermograms of the as-blended La$_2$O$_3$-B$_2$O$_3$-Ca powders and those mechanochemically synthesized for different durations up to 3 h are illustrated in Figs. 7(a)–(g). DSC analyses conducted on the as-blended and milled powders suggest about the thermal behaviors of the samples and the reaction completion. As seen in Fig. 7(a), the DSC curve of the as-blended powders have a small endotherm peaking at about 330 °C and a broad endotherm peaking at about 525 °C, which respectively correspond to the dehydration of small amount of H$_3$BO$_3$ in the structure of B$_2$O$_3$ and the decomposition of Ca(OH)$_2$ into CaO by releasing water. The broad endotherm emerged between the temperature range of 420 and 595 °C could include the partial melting of B$_2$O$_3$ (T$_{melting}$: 450 °C) and residual Ca(OH)$_2$ (T$_{melting}$: 580 °C). Furthermore, as-blended powders have three respective small exotherms with a maximum point at about 690, 820 and 1010 °C (Fig. 7(a)), indicating the formations of calcium borate phases in different compositions (Erfani et al., 2012) and the emergence of LaB$_6$ phase since there are La$_2$O$_3$, B$_2$O$_3$ and CaO phases in the structure of the sample after heating up to the end point of the broad endotherm. On the basis of Figs. 7(b), (c) and (d), 30 min, 45 min and 1 h milling cause shifts in the temperatures of the endothermic and exothermic peaks. In other words, milled powders up to 1 h have the same endothermic and exothermic peaks with those of as-blended one, corresponding to the dehydration of H$_3$BO$_3$ and Ca(OH)$_2$ and formation of calcium borate and lanthanum hexaboride phases, with a significant difference in their peaking temperatures. As compared with Fig. 7(a), the temperature difference in the peaking points of the broad endotherm and three exotherms is respectively about 55, 110, 115 and 155 °C for the 1 h milled powders (Fig. 7(b)). However, the peaking points of the endotherm and consecutive exotherms change with a maximum value of 20 °C, as milling duration increases from 30 min to 1 h (Figs. 7(b)–(d)). It can be said that milling process incredibly changes the thermal behavior of the La$_2$O$_3$-B$_2$O$_3$-Ca powders, if DSC curve of the as-blended powders (Fig. 7(a)) are compared with those in Figs. 7(b)–(d). Milling provides an homogeneous distribution of particles throughout the microstructure and hence the reactivity of the touching particles increases to form calcium borate and lanthanum hexaboride phases. Since as-blended, 30 min, 45 min and 1 h milled powders comprise La$_2$O$_3$, Ca(OH)$_2$ and B$_2$O$_3$ phases (Figs. 5(a)–(d)), general appearance of their DSC thermograms resemble each other, excluding the peaking temperatures. Figs. 7(e)–(g) only shows the broad endothermic peaks respectively at about 445, 440 and 410 °C, pertinent to the dehydration of Ca(OH)$_2$. Since 1.5 h milled powders contain LaB$_6$, CaO, Ca$_3$(BO$_3$)$_2$ and Ca(OH)$_2$ phases, its DSC curve only exhibits the dehydration endotherm, as compatible with the XRD pattern in Fig. 5(e). The heat flow of the broad endotherm decreases as milling duration increases from 1.5 to 3 h, as seen in Figs. 7(e)–(g). After the reaction took place at the end of 1.5 h, the DSC curves do not include any exotherms belonging to the formation of calcium borates and lanthanum hexaboride. Although 2 and 3 h milled powders had LaB$_6$, CaO and Ca$_3$(BO$_3$)$_2$ phases according to the XRD patterns in Figs. 5(f) and (g), the presence of adsorbed Ca(OH)$_2$ was proved by its dehydration endotherms in Figs. 7(f) and (g).

The contradiction between the outcomes of the XRD and DSC analyses arises from the amount of Ca(OH)$_2$ which is below the detection limit of XRD (< 2 wt.%). Similarly in the La$_2$O$_3$-B$_2$O$_3$-Mg system, DSC thermogram of the powders milled for 2 h 45 min, in which reaction was assumed to take place completely according to the XRD
analysis, shows a very small and narrow exotherm peaking at 651 °C corresponding to the oxidation of residual Mg in the powder blend (Ağaoğulları et al., 2012b).

The XRD patterns of the mechanochemically synthesized La$_2$O$_3$-B$_2$O$_3$-Ca powders after DSC analyses up to 1100 °C are given in Figs. 8(a)–(e). The powders milled for 45 min, 1 h, 1.5 h, 2 h and 3 h were subjected to the subsequent XRD analyses in order to detect the existing phases after heating since as-blended powders and those milled for 30 min adhered into the alumina crucible during DSC experiments and hence they could not be discharged from the crucible. As seen in Figs. 8(a) and (b), the powders contain CaO, Ca$_3$(BO$_3$)$_2$ and CaB$_2$O$_4$ (ICDD Card No: 72-1859, Bravais lattice: primitive orthorhombic, a = 0.838 nm, b = 1.382 nm, c = 0.501 nm) phases with a very small amount of LaB$_6$ phase after 45 min or 1 h milling and heating processes. Heating up to 1100 °C results in the formation of a new borate phase, CaB$_2$O$_4$, in addition to the Ca$_3$(BO$_3$)$_2$ which is already obtained after mechanochemical synthesis. Erfani et al. (2012) also obtained CaB$_2$O$_4$ phase after heating the reactants between 750 and 900 °C, which corresponds to the same temperature interval of borate formations in the DSC curves in Figs. 7(a)–(d). After 1.5 h milling and heating, the intensities of the phases, especially that of LaB$_6$, get higher (Fig. 8(c)) and this increasing tendency continues as milling duration increases up to 3 h (Figs. 8(d) and (e)). These findings conform well to the results of the XRD analyses in Figs. 5(e)–(g) and DSC analyses in Figs. 7(e)–(g).

Since La$_2$O$_3$-B$_2$O$_3$-Ca powders milled for 45 min and 1 h contain La$_2$O$_3$, B$_2$O$_3$ and Ca(OH)$_2$ phases (Figs. 5(c) and (d)) after mechanochemical synthesis, they react to form LaB$_6$, CaO, Ca$_3$(BO$_3$)$_2$ and CaB$_2$O$_4$ phases by the effect of applied external heat. However, the desired LaB$_6$ phase is too few in the composition. Only heating up to 1100 °C without a holding time does not result in a complete conversion of the reactants even if short milling duration was conducted on the powders providing a homogeneous microstructure. Moreover, the powders mechanochemically synthesized for 1.5 h and for longer times as 2 and 3 h have already LaB$_6$, CaO and Ca$_3$(BO$_3$)$_2$ phases before heating (Figs. 5(e)–(g)) and it is expected to get increase in their intensities by the effect of heating which ensures grain growth. Although any exotherm indicating Ca borate formation were not detected in the DSC thermograms of the powders mechanochemically synthesized for 1.5, 2 and 3 h in Figs. 7(e)–(g), an amount of CaB$_2$O$_4$ phase occurred in the powders after heating (Figs. 8(e)–(e)). The emergence of CaB$_2$O$_4$ phase can be attributed to the decomposition of Ca$_3$(BO$_3$)$_2$ with the applied heat, in regard of the reaction in Eq. (7).

$$\text{Ca}_3(\text{BO}_3)_2 \rightarrow \text{CaB}_2\text{O}_4 + 2\text{CaO} \quad (7)$$

Although the heating temperature is a little lower than the melting temperature of Ca$_3$(BO$_3$)$_2$ phase obtained after mechanochemical reaction for 1.5 h, an amount of it can decompose during heating by the effect of mechano-
La$_2$O$_3$-B$_2$O$_3$-Ca powder blends, the heating process has resulted in the formation of lanthanum borates when exposed to high temperature. The results indicate that if milling is not carried out on the La$_2$O$_3$-B$_2$O$_3$-Ca powder blends, the heating process has only chance of LaB$_6$ incubation with additional borate compounds. The way of obtaining complete conversion of the reactants is to carry out milling process for longer durations than 2 h or to apply heating on these milled samples with a holding time. Therefore, the significance of the mechanochemical synthesis and its effect on the reduction mechanism of La$_2$O$_3$-B$_2$O$_3$-Ca powder system can be emphasized once more by means of the XRD patterns and DSC thermograms given in Fig. 5 through Fig. 8. Similarly, an amount of LaBO$_3$, Mg$_3$B$_2$O$_6$ and MgO phases occurred in the as-blended La$_2$O$_3$-B$_2$O$_3$-Mg powders in addition to LaB$_6$, after heating up to 1200 °C (Ağaoğulları et al., 2012b). In magnesiothermic reduction, the formation of borate phases arose from both reducing agent and lanthanum source. However, the emergence of LaBO$_3$ phase were not detected in any step of the analyses. This can be evaluated as an advantage of the calciothermic reduction since its reaction does not consume the lanthanum oxide source to form borate, instead of that reducing agent participates in the generation of borates. The higher tendency of yielding Ca borates rather than that of La provides the generation of LaB$_6$ from all La$_2$O$_3$ reactant, after heating.

After the detailed characterizations of the as-blended and mechanochemically synthesized La$_2$O$_3$-B$_2$O$_3$-Ca powders, it can be stated that LaB$_6$ and CaO products are compatible with the reaction in Eq.(1). However, the presence of Ca$_3$(BO$_3$)$_2$ or CaB$_2$O$_4$ (after heating) conflicts with the theoretical reaction. Following the mechanochemical synthesis, reaction products should be purified to achieve fine-grained powders without any or with tolerable contaminations. Thus, leaching treatment was conducted on the powders mechanochemically synthesized for 3 h which contain LaB$_6$, CaO, Ca$_3$(BO$_3$)$_2$ and a very small amount of adsorbed Ca(OH)$_2$ according to the XRD (Fig. 5(g)) and DSC (Fig. 7(g)) analyses.

Fig. 9(a) is the XRD pattern of the La$_2$O$_3$-B$_2$O$_3$-Ca powders after mechanochemical synthesis for 3 h and leaching with 4 M HCl. As seen from the pattern, leached powders contain LaB$_6$ with a very slight and insignificant amount of Ca$_3$(BO$_3$)$_2$. Leaching with 4 M HCl solution provides the complete removal of CaO and Ca(OH)$_2$ in regard of reactions in Eqs. (2)–(4) and also results in the partial removal of Ca$_3$(BO$_3$)$_2$ phase. Due to the fact that some parameters of the leaching process such as solid-to-liquid ratio, leaching temperature and duration, centrifuging duration and speed, etc. were well-chosen, any CaCl$_2$, CaCl$_2$·xH$_2$O and CaOHCl phases do not remain in the structure of the final powders as a leaching product. Furthermore, the AAS analysis of the supernatant liquid decanted from the leached powders gives the elemental results of 5710 ppm Ca, 309.3 ppm B and 3.76 ppm Fe. The Ca element in the supernatant liquid arises from the complete dissolution of CaO and the partial dissolution of Ca$_3$(BO$_3$)$_2$. So, the amount of Ca is lower than the expected amount since there is still remaining Ca$_3$(BO$_3$)$_2$ phase in the leached powders. It is believed that the presence of B element in the supernatant liquid can only arise from the slight dissolution of LaB$_6$ phase in the concentrated HCl solution since there is no unreacted B$_2$O$_3$ phase in the 3 h mechanochemically synthesized powders as verified by the DSC analysis in Fig. 7(g).

Fig. 9(b) shows the XRD pattern of the commercial LaB$_6$ powders (Alfa Aesar$^{TM}$, in purity of 99.5 %, with an average particle size of 4 µm). It can be obviously seen that there is not any observable contamination in the commercial LaB$_6$ powders and their intensities are higher than those of laboratory-synthesized one, comparing the XRD patterns in Figs. 9(a) and (b). Besides, the production method of commercial LaB$_6$ powders is not known. Due to obtain uncontaminated LaB$_6$ powders having an XRD pattern similar to that of commercial one, additional treatments should be carried out or concentration of HCl should be increased.

Fig. 10(a) is the SEM image of the La$_2$O$_3$-B$_2$O$_3$-Ca powders after mechanochemical synthesis for 3 h, in which rounded-shaped particles having sizes below 3 µm can be easily seen. Although the XRD pattern of the 3 h...
milled powders revealed the presence of LaB₆, CaO and Ca₃(BO₃)₂ phases (Fig. 5(g)), there are also white dendritic Ca(OH)₂ phases adsorbed on the small rounded-shaped particles, which agrees very well with the DSC analysis in Fig. 7(g). The dendritic Ca(OH)₂ phase was also detected in a previous study related with the synthesis of CaB₆ powders via mechanochemical reaction of Ca-B₂O₃ blends (Balcı et al., 2012). Figs. 10(b) and (c) show the SEM images of the La₂O₃-B₂O₃-Ca powders after mechanochemical synthesis for 3 h and leaching with 4 M HCl, in different magnifications. SEM images illustrate the rounded-shaped LaB₆ particles together with the embedded Ca₃(BO₃)₂, ranging in sizes between 250 nm and 1 µm. Since Figs. 10(a) and (b) have the same magnification scale, it is evident to comprehend the effect of leaching on the 3 h milled powders. Before leaching treatment, Ca-based particles (CaO, Ca₃(BO₃)₂ and Ca(OH)₂) hold the LaB₆ particles together and it results in an agglomerated microstructure in which the presence of smaller particles can not be observed (Fig. 10(a)). Besides, leached powders do not consist of perfect spheroidal-shaped particles throughout the structure (Figs. 10(b) and (c)) because the repeated fracturing and repeated welding mechanism changed their morphologies during milling (Suryanarayana, 2001). After leaching, there is still agglomeration between the particles due to the existence of Ca₃(BO₃)₂ phase (Figs. 10(b) and (c)) and the measured size range of the particles monitored by SEM can result in misleading results. So, the average particle size of the leached powders was accurately determined under the effect of ultrasonic homogenizer. PSA graph in Fig. 10(d) displays the average size of the leached particles as about 80 nm.

As a result of analyses carried out after leaching treatment, it can be interpreted that Ca has an excessive tendency to form borate phases which can be completely eliminated by leaching with excess HCl in concentration above 4 M. Also, it is comprehensible that higher concentrations of HCl can cause the higher dissolution of synthesized LaB₆ phase at the same leaching conditions and so this can result in more decrease in the LaB₆ intensities. However, 6 M HCl was also used in order to remove undesirable Ca₃(BO₃)₂ phase for obtaining pure LaB₆ powders. Fig. 11 represents the XRD pattern of the La₂O₃-B₂O₃-Ca powders after mechanochemical synthesis for 3 h and leaching with 6 M HCl. As seen from Fig. 11, 6 M leached powders have only LaB₆ phase without any detectable contamination. AAS analysis of the supernatant liquid decanted from these leached powders gives the amounts of the elements as 5820 ppm Ca, 356.4 ppm B and 3.78 ppm Fe. In comparison with the elemental results of 4 M leached powders, the amounts of Ca and B increase significantly, indicating the disappearance of Ca₃(BO₃)₂ phase in the powder composition and the dissolution of LaB₆ phase. Thus, the XRD pattern of the 6 M leached powders (Fig. 11) and also AAS analysis of the decanted supernatant liquid demonstrate that final LaB₆ powders are sufficiently pure and they do not contain any remnants of residual elements during HCl leaching. Dis-
simply, 3.6 M HCl is enough to remove all undesirable MgO in the milled La2O3-B2O3-Mg powders due to the absence of Mg borate phase in the microstructure (Ağaoğulları et al., 2012a).

Figs. 12(a) and (b) are the bright-field (BF) micrographs taken from the La2O3-B2O3-Ca powders after mechanochemical synthesis for 3 h and leaching with 6 M HCl. Fig. 12(a) shows both polygonal/spheroidal-shaped and equiaxed-shaped particles in sizes varying between 50 and 350 nm. Moreover, different morphologies of the particles arising from the milling mechanism can be distinctly observed from the BF image of the powders in higher magnification given in Fig. 12(b). In comparison with Fig. 12(a), the presence of smaller particles with an average size of 20 nm is proved in Fig. 12(b). Fig. 12(c) displays the corresponding general EDS measurement taken from the particles in BF image (Fig. 12(b)).

EDS measurement reveals that there is 69.15 ± 1.60 wt.% La and 30.85 ± 0.75 wt.% B in the composition of the particles indicating the existence of LaB6 phase, which is consistent with the amounts of elements in the stoichiometric phase. The detected Cu element arises from the copper grid on which the powders were supported. EDS results also prove that any contamination originating from the unwanted Ca3(BO3)2 phase does not remain in the structure after 6 M leaching treatment, which is in good agreement with XRD analysis in Fig. 11. Consequently, pure LaB6 powders were obtained from La2O3-B2O3-Ca powders after mechanochemical synthesis for 3 h and leaching with 6 M HCl, having particles in size between 20 and 350 nm.

Calciothermic reduction of La2O3 and B2O3 containing powder blends by mechanochemistry at room temperature can be an alternative method for the preparation of nano-sized LaB6 powders in high purity, rather than magnesiothermic reduction methods and other conventional production techniques.

4. Conclusions

In this study, nanosized LaB6 powders were successfully synthesized from the related oxides of the elements, via calciothermic reduction by mechanochemistry performed at room temperature. Based on the results reported in the present study, the following conclusions can be drawn:

- After mechanochemical synthesis of the La2O3-B2O3-Ca powder blends in Spex™ 8000D Mixer/Mill using a 10:1 BPR for 1.5 h, LaB6, CaO and Ca3(BO3)2 phases were obtained in addition to very small
amounts of unreacted La$_2$O$_3$ and Ca(OH)$_2$.

- XRDA analyses showed that extending the milling duration to 2 h resulted in a complete reaction in which unreacted La$_2$O$_3$ and Ca(OH)$_2$ phases disappeared and the composition only contained LaB$_6$, CaO and Ca$_3$(BO$_3$)$_2$ phases. Besides, calciothermic reduction by mechanochemistry was achieved 45 min earlier than that of magnesiothermic one.

- All mechanochemically synthesized powders had the same LaB$_6$, CaO, Ca$_3$(BO$_3$)$_2$ and CaB$_2$O$_4$ phases after heating up to 1100 °C and there was an increasing tendency in the occurrence of the phases as the milling duration increased.

- LaB$_6$ phase synthesized during mechanochemical reactions (≥ 1.5 h) are thermally very stable since they have not any tendency to transform into an amount of lanthanum borate phases when exposed to high temperature.

- DSC results indicated that if longer milling durations were not applied on the La$_2$O$_3$-B$_2$O$_3$-Ca powder blends, the heating process of powders only yielded the incubation of LaB$_6$ with additional Ca borate compounds.

- DSC and SEM analyses exhibited that a dendritic Ca(OH)$_2$ phase adsorbed on the LaB$_6$, CaO and Ca$_3$(BO$_3$)$_2$ particles in the microstructure of the 2 and 3 h milled powders, which can be easily eliminated by HCl leaching.

- LaB$_6$ powders were obtained with an average particle size of 80 nm and in the presence of very small amount of Ca$_3$(BO$_3$)$_2$ phase from La$_2$O$_3$-B$_2$O$_3$-Ca powder blends after mechanochemical synthesis for 3 h and leaching with 4 M HCl.

- Pure LaB$_6$ powders were obtained from La$_2$O$_3$-B$_2$O$_3$-Ca powders after mechanochemical synthesis for 3 h and leaching with 6 M HCl, having particles in size between 20 and 350 nm.

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Nomenclature

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<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>AAS</td>
<td>Atomic Absorption Spectrometer</td>
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<td>BF</td>
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<td>BPR</td>
<td>Ball-to-Powder Weight Ratio</td>
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<td>Self-propagating High-temperature Synthesis</td>
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