Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Low temperature carbothermal and boron carbide reduction synthesis of LaB₆

Muhammad Hasan, Heber Sugo, Erich Kisi*

School of Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia

ARTICLE INFO

Article history: Received 18 February 2013 Received in revised form 1 May 2013 Accepted 2 May 2013 Available online 9 May 2013

Keywords: Hexaborides Lanthanum hexaboride Synthesis Thermionic emission

ABSTRACT

Rare-earth hexaborides are widely used as thermionic emitters however their economic production for large scale applications such as solar thermionic electricity generation is hampered by a need to synthesise them at lower temperature without post-synthesis cleaning treatments. Two simple synthesis techniques for producing pure lanthanum hexaboride (LaB₆), carbothermal reduction using La₂O₃-boroncarbon and boron carbide reduction using La₂O₃-B₄C blends respectively were studied. Using fine grained starting materials and a mild pre-milling treatment, the carbothermal method was found to produce high-purity LaB₆ at a temperature 1400 °C or below. The B₄C method also appeared from XRD and SEM analyses of abraded surfaces to produce high-purity LaB₆ at 1400 °C however EDS maps of polished cross-sections revealed the presence of unreacted B₄C necessitating a temperature of 1450 °C to complete the reaction. XRD and SEM analyses indicate that the mean particle sizes of LaB₆ using the boron carbide method (220 nm) is smaller than that for the carbothermal reduction method (600 nm). The finer grains of samples prepared via the boron carbide method result in a partially sintered powder. LaB_6 prepared in this way is shown to have a Richardson work function of 2.64 eV.

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1. Introduction

Rare-earth hexaborides (ReB₆) are attractive for high temperature applications involving thermionic emission due to their high emissive yield (low work function, high electrical conductivity, etc.) and long lifetime (high melting point and superior chemical stability) [1,2]. Due to these unique properties, refractory ceramics ReB₆ are also used in applications such as field-electron emitter sources in various devices [3,4], as sensors in high-energy optical systems [5] and as decorative and thermionic coatings [6]. In a pioneering work, Lafferty [2] thoroughly investigated the thermionic emission properties of different hexaborides and found lanthanum hexaboride (LaB₆) to be the best thermionic emitter due to a low evaporation rate at higher temperature. LaB₆ possesses the lowest vapor pressure among the rare-earth hexaborides [7]. The structure of all rare-earth hexaborides including LaB₆ is a cubic CsCl-like arrangement in space group *Pm3m*, in which a single lanthanum atom occupies the origin site and a cluster of six boron atoms occupies the octahedral site [8–10]. The strong covalent bonding of boron in the structure makes the material very hard [10,11].

To date, a good number of synthesis routes have been explored to prepare LaB₆, such as: carbothermal reduction of lanthanum oxide (La₂O₃) using boron and carbon [12,13]; borothermal reduc-

* Corresponding author. Tel.: +61 2 49 216213. E-mail address: Erich.Kisi@newcastle.edu.au (E. Kisi). tion of La_2O_3 and B [13–15]; boron carbide reduction of La_2O_3 and boron carbide (B_4C) [13]; and an aluminum flux method using La, B and Al or La₂O₃, B₂O₃ and Al [16-18]. The foregoing research reported the preparation of LaB₆ using these methods at high temperatures in the range 1500–1800 °C. In industry, both carbothermal and boron carbide methods are widely used due to simple solid-state reactions among the commonly available reactants lanthanum oxide, boron and carbon or lanthanum oxide and boron carbide. Recently, a wide variety of new routes such as combustion synthesis [19-21], mechano-chemical synthesis [22], high pressure chemical reactions in closed cells or autoclaves [10,23,24] and vapor phase reaction [25] have been employed to synthesise LaB₆ at lower temperatures (250–1200 °C). The main drawback for most of these methods is that they require considerable post-synthesis treatment to obtain pure LaB₆. The synthesis route using vapor phase reaction employs gaseous BCl3 and lanthanum precursors to prepare LaB₆ at a low temperature 1000-1200 °C [25,26], however, gaseous BCl₃ is highly prone to absorb moisture and convert to boric acid. In addition, the stoichiometry of the products is difficult to maintain. Another low-temperature synthesis route (250-900 °C) uses high-temperature and highpressure autoclaves [27]. The reaction in this process cannot be directly observed due to the use of the autoclave which makes the fundamental understanding of this technique difficult. Moreover, this process can result in highly agglomerated powders due to the long processing times.





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Fig. 1. Microstructures of the starting materials: (a) La₂O₃, (b) B, (c) B₄C and (d) graphite.

The grain size of the as-prepared LaB₆ plays a vital role for subsequent sintering into dense components. It is reported that LaB₆ having fine grain size shows enhanced thermionic emission compared with that having coarse grains [28]. Using the traditional preparation methods, it is usual to obtain greater than micronsized lanthanum hexaborides whereas the newer synthesis routes mostly result in LaB₆ having sub-micron sized particles. Although the finer grain size and lower processing temperature of the newer methods is advantageous, they are costly to implement and require post-synthesis treatments to purify the products. The preparation of nanostructured LaB₆ at a comparatively low temperature without any post-synthesis treatments using the carbothermal or boron carbide method is considered to represent a significant advancement.

Therefore, in the present work, carbothermal and boron carbide reduction methods for LaB₆ preparation have been investigated using fine lanthanum oxide and boron powders with standard graphite and boron carbide powders as starting materials without any post-synthesis treatments. Structural, morphological and chemical properties are presented for samples synthesised at different temperatures and durations under moderate vacuum conditions. Thermionic properties of the as-synthesised LaB₆ were determined using a Schottky device in the temperature range 950–1200 °C.

2. Experimental details

In this study, the raw materials used were La₂O₃ powder (Sigma–Aldrich Co., USA, 99.9% purity, particle size 1–3 µm), technical grade amorphous boron powder (Sigma–Aldrich Co., Germany, 95–97% purity, particle size 1–5 µm), boron carbide (Alfa Aesar Co. UK, 99+% purity, particle size <10 µm) and graphite (Sigma–Aldrich Co., USA, 99.99% purity, particle size <150 µm). EDS on the raw materials reveals that Si and Fe in trace amounts are present in boron and boron carbide, respectively. Fig. 1 shows the microstructure of the raw materials. From the figure, both boron and lanthanum oxide are found to have particles with a mean size from a few hundred nanometers to a few microns. Due to fine particle size of La₂O₃ and its strongly hygroscopic nature, La₂O₃ is prone to hydrolyze into La(OH)₃ upon even moderate exposure to laboratory air. Although the material used in this work was stored and weighed as La₂O₃ in a dry argon atmosphere, subsequent conversion to La(OH)₃ during handling and milling was observed by XRD and its effects discussed later.



Fig. 2. XRD patterns of milled powders and raw constituents before milling for (a) the carbothermal and (b) the boron carbide method.

In order to investigate the effect of La₂O₃ and La(OH)₃ as reactants, additional samples were prepared using material calcined at 1000 °C and under protective atmosphere at all times.

Two synthesis routes for LaB_6 were attempted in this study. For the carbothermal route, powder blends containing stoichiometric amounts of dry reactants were mixed by milling for 30 min with ball-to-powder ratio of about 5:1 in a SPEX8000 mixer mill according to the overall reaction given in the following equation:

$$La_2O_3 + 12B + 3C \rightarrow 2LaB_6 + 3CO \tag{1}$$

For each run, powder batches of 5 g were weighed out using stoichiometric amounts of La_2O_3 and B. Graphite was added in excess of the stoichiometric ratio by 16–19%. The second synthesis route used boron carbide to decompose the La_2O_3 . Stoichiometric amounts of reactants were also mixed by milling for 20 min according to the overall reaction in the following equation:

$$La_2 + 3B_4C \rightarrow LaB_6 + 3CO \tag{2}$$

Subsequently, both types of mixed powders were pressed into cylindrical pellets under pressures of 60–100 MPa. The pellets were then placed into a graphite crucible within a horizontal tube furnace lined with graphite foil. The reaction was performed under a moderate vacuum (below 0.1 Pa) at different temperatures in the range 1250–1500 °C for 4 or 8 h. The heating and cooling rates were maintained within the range 2–4 °C/min. Prior to XRD and SEM, the surface of the as-prepared samples was abraded to a depth of 0.5–1.0 mm using SiC abrasive paper to remove the surface impurities. The types of surface impurities depend on the environment of the tube furnace and diffusion of different volatile materials from the inner part of the pellets.

The phases present in the samples were analyzed by X-ray diffraction (Panalytical X'pert MPD) using Cu K α radiation (λ = 0.15406 nm) and operating at an accelerating voltage of 40 kV and emission current of 40 mA with scan rate of 0.03°/s and step size 0.008°. Phase identification utilized the ICDD database. The crystallite size of the samples was calculated using the Scherrer equation:

$$D = \frac{0.89\lambda}{B\cos\theta} \tag{3}$$

where *D* is the mean crystallite diameter, λ the X-ray wavelength, *B* the broadening of the full-width at half-maximum of the diffraction peak (FWHM), and θ the diffraction angle.

Rietveld analysis of the XRD patterns was performed for data in the range between 20° and 80° 2 θ using the Rietica software (Windows version 1.77) written by Hunter and Howard [29]. Typically, the refined parameters include a polynomial background; 2 θ zero offset; scale factor and lattice parameters for each phase present; and atom coordinates and peak width parameters for the major phase(s). The refined scale factors were used to conduct Quantitative Phase Analysis (QPA) according to the method of Hill and Howard [30].

The surface morphology of the samples was characterized using SEM and backscattered electron imaging. Chemical composition was assessed by means of energy dispersive X-ray analysis (EDS) using a Philips XL30 SEM with Oxford ISIS EDS system at accelerating voltages of 15–25 kV. Imaging, elemental mapping and EDS were also performed on abraded and polished samples using a ZEISS Sigma FESEM at accelerating voltages of 3–15 kV.

Finally, work function measurement was performed using a typical pure LaB₆ sample in a Schottky device in the temperature range of 950–1200 °C. The gap between the emitter and the collector was maintained at about 2.5 mm. The collector



Fig. 3. XRD patterns for samples prepared at different temperatures using the carbothermal method.

itself had a diameter of 6 mm. DC emission testing was carried out by applying accelerating voltages in the range of 0–400 V. Schottky plots and a Richardson plot were used to find the Richardson work function of the as-synthesised lanthanum hexaboride pellet.

3. Results and discussion

To understand the effects of ball milling, X-ray diffraction patterns were collected from the starting materials and the milled powders. Patterns for the starting powders are shown in the lower parts of Fig. 2a and b for the carbothermal and boron carbide methods respectively. The La_2O_3 powder was well crystallised and contained a very small amount of $La(OH)_3$. The B₄C and graphite powder showed good crystallinity with the expected preferred orientation in the latter and some peak broadening due to small crystallite size. The boron was found to be poorly crystalline.

Fig. 2a and b also shows XRD patterns for the milled powders and their respective constituents. It may be seen that the La_2O_3 has hydrolyzed to $La(OH)_3$ during handling and milling with only minor amounts of La_2O_3 and a trace of $La_2O_2CO_3$ present as second phases. The average crystallite size of $La(OH)_3$ for both methods was found to be about 30 nm compared with the average



Fig. 4. XRD patterns for different samples prepared at different temperatures using the boron carbide method.



Fig. 5. Variation of mean crystallite size of LaB_6 particles with synthesis temperature. Lines are a guide to the eye only.

crystallite size for the original La_2O_3 which was found to be approximately 262 nm. These observations imply that the milled material is finer and more active, subsequently reacting with CO_2 to form $La_2O_2CO_3$. In the case of the boron carbide method, much less $La_2O_2CO_3$ was found to form as shown in Fig. 2b.

X-ray diffraction patterns from pellets prepared using carbothermal reduction of La₂O₃ by boron and carbon at temperatures in the range 1250-1400 °C are shown in Fig. 3. All of the XRD patterns are dominated by the regularly spaced LaB_6 peaks. It may be seen from the pattern of the sample prepared at 1250 °C that the synthesis proceeds via an intermediate compound; lanthanum borate (LaBO₃) which has signature diffraction peaks around $25^{\circ} 2\theta$. LaBO₃ is the only intermediate phase observed during the carbothermal reduction method in the temperature range 1250-1400 °C. Samples prepared at 1300 °C were almost pure LaB₆ with only a small amount of LaBO₃ or carbon being present. Samples prepared at 1350 °C exhibit a single LaBO₃ peak barely noticeable above background in the XRD pattern whilst samples prepared at 1400 °C show no peaks other than those for LaB₆. In the present work, the temperature (1350-1400 °C) required for preparing reasonably pure lanthanum hexaboride via the carbothermal reduction method is well below the value (1500 °C) reported in earlier work using the same method [12]. Samples prepared using freshly calcined La₂O₃, handled only in argon and reacted at 1350 °C gave essentially identical results to those above indicating that conversion of La₂O₃-La(OH)₃ is not the cause of the lower reaction temperature.

In the other synthesis technique, the boron carbide method $(La_2O_3 \text{ and boron carbide})$ was employed for preparing LaB_6 . Fig. 4 shows the XRD patterns for the pellets prepared at different temperatures having holding times of 4 h or 8 h. LaB₆ is clearly present as a major phase in all the samples, even those prepared as low as 1200 °C. All the samples prepared below 1400 °C exhibit the intermediate phase lanthanum borate (LaBO₃). The sample prepared at 1400 °C appears to be impurity free however, some small signature peaks of LaBO₃ and boron carbide were observed in an XRD pattern taken from the central part of a sample prepared at this temperature. This effect will be further discussed below. The samples prepared at a temperature below 1300 °C also show, in addition to LaBO₃, some characteristic peaks for boron carbide and/or lanthanum carbide. From the XRD patterns, it can be concluded that the boron carbide method requires a minimum temperature of 1400 °C to produce pure LaB₆. One of the observed impurities in the starting material of boron carbide, particularly Fe, shows its presence in the form of iron boride (FeB) for the samples prepared at higher temperatures (1400–1500 °C). Once again, samples prepared using calcined La₂O₃ and handled only in argon gave essentially identical results to those above when reacted at 1400 °C.

Fig. 5 shows trends in the average crystallite size of LaB₆ calculated from Scherrer's equation for the carbothermal and boron carbide methods. The crystallite size for the carbothermal method is higher than that from the boron carbide method. For the boron carbide method, the crystallite size increases slowly with increase of temperature up to 1350 °C and increases dramatically at 1400 °C. The mean crystallite size for lanthanum hexaboride samples prepared at 1400 °C using carbothermal and boron carbide methods were found to be approximately 600 nm and 220 nm, respectively. LaB₆ powder with a particle size between 75 and 300 nm has been reported recently using prolonged high-energy milling of lanthanum oxide, boron and magnesium [22].

Rietveld analysis based on the diffraction data was carried out for all patterns of the samples prepared by the carbothermal method using the standard structural models for LaB₆, LaBO₃ and C. Fig. 6 shows an example of the refinement plot for a sample prepared at 1300 °C. After the final refinement for the example shown



Fig. 6. The calculated (red, solid line) and observed (+) XRD patterns and their difference (green solid line below) for a sample prepared at 1300 °C by the carbothermal method: Vertical bars below show positions for all possible Bragg peaks for LaB₆, LaBO₃ and graphite respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Temperature (°C)	% By mass(molar) – carbothermal method			% By mass(molar) – boron carbide method			
	LaB ₆	LaBO ₃	С	LaB ₆	LaBO ₃	B ₄ C	LaC ₂
1200	-	-	-	26.7(18.3)	50.5(35.6)	16.0(40.3)	6.8(5.8)
1250	73.1(65.0)	26.1(24.0)	0.7(11.0)	47.5(35.0)	39.1(29.6)	12.9(34.9)	0.6(0.5)
1300	93.9(92.9)	6.1(6.2)	0.1(0.9)	57.4(46.5)	31.1(25.9)	8.0(24.0)	3.5(3.6)
1350	99.4(98.5)	0.6(0.6)	0.1(0.9)	78.1(67.4)	16.2(14.4)	5.7(18.2)	0(0)
1400	99.9(99.9)	0.1(0.1)	0(0)	99.8(99.5)	0(0)	0.1(0.5)	0(0)
1450			_	99.9(99.6)	0(0)	0.1(0.4)	0(0)
1500	-	-	-	100(99.9)	0(0)	0(0.1)	0(0)

 Table 1

 Quantitative phase analysis using Rietveld refinement of the samples prepared using different methods.

in Fig. 6, the agreement indices were $R_p = 4.78\%$, $R_{wp} = 6.19\%$, and $\chi^2 = 1.01$ respectively, indicating that the quality of the agreement between calculated and observed intensities is excellent. Standard structural models for LaB₆, LaBO₃, B₄C and LaC₂ were also utilized for Rietveld refinements of the samples prepared using the boron carbide method. Quantitative analyses based on the Rietveld refinements for all sample types are given in Table 1. The table shows that according to XRD anlaysis lanthanum hexaboride of high purity (99.9% or above) can be achieved by carbothermal and boron carbide methods at synthesis temperatures of 1400 and 1500 °C, respectively.

From Table 1 and Fig. 3, it appears that using the carbothermal method, LaB₆ having a purity above 99% by weight can be obtained at a temperature as low as 1350 °C. To obtain lanthanum hexaboride of the same purity using the boron carbide method, a slightly higher temperature of 1400 °C is required. Fig. 7a shows the percent conversion of LaB₆ with temperature for both methods. From this figure, it is observed that the percent conversion from lanthanum compounds to LaB₆ for the carbothermal method is greater at lower temperatures in agreement with qualitative observations. A linear trend for the synthesis of LaB₆ using the boron carbide method can be observed between 1200 and 1400 °C. Variation in the lattice parameter of primitive cubic LaB₆ with temperature is shown in Fig. 7b. The carbothermal method produces LaB₆ with a consistent value for lattice constant (*a*) of 4.15745(6) Å. In comparison, the LaB₆ produced by the B₄C route shows a small fluctuation of the lattice parameter between 4.157 and 4.158 Å at synthesis temperatures between 1200-1400 °C. At higher temperatures, a constant value of 4.15733(6) Å is produced. From the above, it can be inferred that the variation of the lattice constant for both methods is insignificant and the values agree with the value (4.1570 Å) for the standard LaB₆ data from ICDD (JCPDF No. 073-1669).

Microstructural morphology was investigated under an SEM for the samples prepared at 1400 °C via both synthesis routes. Fig. 8 shows the micrographs for these samples. From Fig. 8a, the growth of crystals of LaB₆ is clearly observable. The size of the cubic crystals in the micrograph ranges from 200 nm to a few microns. The average particle size seems to be at a sub-micron level which is



Fig. 7. (a) Percent conversion to LaB_6 and (b) variation of LaB_6 lattice parameter with synthesis temperature. Lines are a guide for the eye only.



Fig. 8. SEM image for pure LaB₆ prepared at 1400 °C using (a) carbothermal reduction method and (b) boron carbide method. The circle in (a) highlights local sintering.

in good agreement with the calculated value (600 nm) using the Scherrer equation. Some sintering of the particles appears to have occurred as indicated by the encircled area. The micrograph for the sample prepared via the boron carbide method as shown in Fig. 8b exhibits crystals of LaB₆. This figure reveals a morphology having irregular shaped LaB₆ particles. It is also observed that the particles are better sintered with a polycrystalline, partly porous structure. The mean particle size of the sample appears to be nanostructured in agreement with the calculated mean value for crystallite size from XRD data mentioned earlier.

EDS maps performed using a high resolution FESEM on the epoxy mounted and polished cross-sections of the samples fired at 1250 °C using both the carbothermal and boron carbide methods confirmed the presence of the intermediate phases found using XRD. Samples prepared at 1400 °C using the carbothermal method showed a uniform distribution of elements typical of a single phase. However, samples produced at 1400 °C via the boron carbide method were inhomogeneous as shown in Fig. 9 by the different elemental mappings and a back-scattered electron (BSE) image. The presence of a small amount of LaBO₃ in the central part of the sample prepared at 1400 °C as discussed earlier is confirmed by the bright area in the oxygen map (Fig. 9e). From the backscattered image in Fig. 9a, the black particles are thought to be the residue of boron carbide particles. These boron carbide particles appear to undergo a topo-chemical reaction that results in lanthanum borate and subsequently lanthanum hexaboride in a shell around the B₄C. The inner parts are found to be boron rich as shown in Fig. 9d and were initially thought to be residual boron only. However the carbon map in Fig. 9f was found to be strongly affected by the epoxy resin within voids and careful EDS spot analyses revealed that the black particles are residual boron carbide having distinct boron and carbon EDS peaks. Considering Fig. 9c-e, it is clear that the rest of the boron is mainly in the form of LaB₆. The contradiction between the XRD results in Figs. 4 and 7, and these cross-sectional EDS results is due to a combination of the topo-chemical nature of the reaction which leads to a film of LaB₆ on the surface of the B₄C particles and the low intensity of X-ray scattering from B and C compared with La – in the approximate ratio 5:6:57 and similarly disproportionate absorption factors. In addition, the boron used as a starting powder was poorly crystalline as demonstrated in Fig. 2. It is therefore necessary to use a higher temperature in the B₄C method (1450 °C) than superficially indicated by the XRD patterns. In the present work, the temperatures required for preparing LaB₆ via carbothermal (1350 °C) or boron carbide reduction (1450 °C) methods are nonetheless significantly lower than the values reported in earlier work (1500 °C and 1650 °C respectively [12,13]). The formation of very fine nanostructured reactant crystallites during milling may play a role in the reduced synthesis temperature for both methods. Using graphite foil lined alumina tube furnace as well as a graphite crucible is also thought to have a positive impact on reducing the synthesis temperature.

As an additional test of the material synthesised, thermionic emission measurements were conducted. Schottky and Richardson plots are most commonly employed to estimate the Richardson work function [31]. Fig. 10a and b shows the Schottky plot (Ln (emission current density, J) versus square root of emitter–collector



Fig. 9. Micrographs of a polished cross-section from a sample prepared at 1400 °C via boron carbide method: (a) BSE image and elemental mappings for (b) all elements, (c) lanthanum, (d) boron, (e) oxygen and (f) carbon.



Fig. 10. (a) Schottky plots at different temperatures and (b) Richardson plot for a typical LaB₆ sample prepared at 1450 $^\circ C$ using the boron carbide method.

voltage, V) and Richardson plot $(Ln(J_0/T^2)$ versus 1000/T), respectively, for the sample prepared at 1450 °C via the boron carbide synthesis route. The slope of the Richardson plot was used to establish that the Richardson work function is 2.64 eV. This measured work function is in good agreement with values reported in the literature [2].

4. Conclusions

It has been demonstrated that simple synthesis routes may be used to prepare reasonably pure LaB₆ at lower temperatures than previously reported. Quantitative phase analyses using Rietveld refinement and cross-sectional SEM shows that the carbothermal method, using a solid-state reaction among boron, lanthanum oxide and carbon produces the hexaboride at a minimum temperature of 1350 °C whilst firing in the region of 1450 °C is required to obtain good quality LaB₆ using B₄C as a source of boron. The mean crystallite size for both carbothermal and boron carbide methods are observed to be below one micron suggesting good sinterability, however, the carbothermal method produces somewhat larger crystallites. At lower temperatures, both methods exhibit the presence of LaBO₃ as an intermediate phase and EDS elemental maps suggest that the reaction using boron carbide proceeds by the topo-chemical consumption of the B₄C. The linear reaction rate implied in Fig. 7a supports this observation. A note of caution must be sounded concerning overreliance on XRD for phase analysis without confirmation using *cross-sectional* EDS maps as in Fig. 9.

Acknowledgements

The authors gratefully acknowledge the financial support given for this work by the Australian Solar Institute (ASI) (Grant No. 1-065). The authors also acknowledge help and support from David Phelan and Jennifer Zobec in the UoN Electron Microscope & Xray Unit, The University of Newcastle.

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