



Low temperature synthesis of low thermionic work function $(\text{La}_x\text{Ba}_{1-x})\text{B}_6$



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ABSTRACT

This study presents investigations of the microstructure, morphology and emission properties of the promising thermionic material $(\text{La}_x\text{Ba}_{1-x})\text{B}_6$. The material was synthesised by solid-state reaction without post-synthesis purifications. Powder X-ray diffraction revealed that samples prepared at a temperature ≥ 1500 °C had formed a significant proportion of solid solution (above 54 mass%). Subsequent sintering at 1950 °C caused the formation of a mixture of three solid solutions with the dominant phase being $(\text{La}_{0.31}\text{Ba}_{0.69})\text{B}_6 \sim 85\%$ (by mass). The Richardson work function and emission constant for this boride mixture were found to be 1.03 eV and 8.44×10^{-6} A cm K^{-2} respectively.

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1. Introduction

Thermionic cathodes are widely used in a variety of thermal emission and field emission devices including cathode ray tubes, sensors and electron microscopes. Each application utilises materials tuned for the specific mode of operation (DC, pulsed *etc.*) and required emission current. Recently, the potential of thermionic energy conversion for concentrated solar electricity generation or industrial waste heat recovery has caused a revival of interest in thermionic emitters for long-term stable DC emission. In terms of material properties, the voltage and power output of a thermionic converter can be maximised by selecting an emitter (cathode) with a moderate work function and high emission constant to yield an appropriate current at the operating temperature. The collector material (anode) should possess a low work function and low emission constant to minimize back emission of electrons. Other properties of the emitter includes high melting temperature, low vapour pressure and high electrical conductivity to sustain high emission currents; properties not often available in a single phase. A case in point are the rare-earth hexaborides (REB_6) which have outstanding thermal stability in vacuum as well as moderate work function (2.5–3 eV).

Numerous pure and mixed hexaborides have been investigated for thermionic or field emission properties including (LaB_6) and other REB_6 [1], $(\text{La}_x\text{RE}_{1-x})\text{B}_6$ [2], $(\text{La}_x\text{Gd}_{1-x})\text{B}_6$ [3], $(\text{La}_x\text{Ce}_{1-x})\text{B}_6$ [4], $(\text{Nd}_x\text{Gd}_{1-x})\text{B}_6$ [5], and $(\text{La}_x\text{Ba}_{1-x})\text{B}_6$ [6–8]. Due to the good

emission characteristics and low evaporation rate at higher temperatures, LaB_6 has been identified to be the best thermionic emitter [1,2] however, barium compounds are often used to reduce the work function of different cathode materials through the formation of a barium monolayer [6,9,10]. As a consequence, the possibility of enhanced thermionic emission properties in lanthanum hexaborides by forming solid-solutions or mixed boride compounds with the general formulae $(\text{La}_x\text{Ba}_{1-x})\text{B}_6$ has also been explored [6–8]. More recent studies have involved the preparation of $(\text{La}_x\text{Ba}_{1-x})\text{B}_6$ using mixtures of lanthanum and barium hydrides with boron followed by processing using spark plasma sintering [7,8] or the aluminium flux method [2]. Zhou et al. [7] reported on a boride mixed in the proportions $(\text{La}_{0.6}\text{Ba}_{0.4})\text{B}_6$. The Richardson work function (ϕ_R) was determined to be 1.95 eV and the Richardson emission constant (A_R) = 1.07 A cm^{-2} K^{-2} . These properties were determined using a cathode area of 0.64 mm^2 under pulsed emission current conditions of 20 μs at 120 Hz between 1500 K and 1873 K. An improvement of $\sim 34\%$ at 1873 K was noted in the emission properties of the $(\text{La}_{0.6}\text{Ba}_{0.4})\text{B}_6$ mixture compared to pure LaB_6 prepared using the spark plasma sintering [7].

Observation of the XRD plot reported by Zhou et al. [7] does not reveal the formation of any significant level of solid-solution between the two compounds. Most likely, this is the result of the very short sintering time (5 min) of the spark plasma sintering technique. Kiparisov et al. [6] using the borothermal reduction method prepared solid-solutions of $(\text{La}_x\text{Ba}_{1-x})\text{B}_6$ (where $x = 0.6$ – 0.7) and reported an improvement of the emission characteristics. In order to explore any possible further enhancement of the

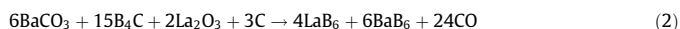
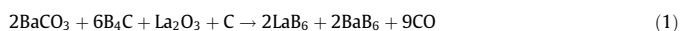
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emission properties by barium substitution into LaB_6 , at higher Ba ratios, attempts to synthesize $(\text{La}_x\text{Ba}_{1-x})\text{B}_6$ solid-solutions using the boron carbide solid-state reduction method are reported in the present work. $(\text{La}_x\text{Ba}_{1-x})\text{B}_6$ cathode materials were fabricated through mechanical milling, pressing, firing and sintering. This work describes the structural, chemical and thermionic properties of the resultant mixed and solid solution boride material.

2. Experimental details

Samples were prepared using: barium carbonate (BaCO_3 , May & Baker Ltd., UK, 99.5 wt% purity), La_2O_3 (Sigma–Aldrich Co., USA, 99.9% purity, particle size 1–3 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) powders. Mixed borides of LaB_6 and BaB_6 were prepared by reducing La_2O_3 and BaCO_3 with boron carbide and graphite using the boron carbide reduction method [11]. Stoichiometric amounts of these raw materials sufficient for samples of ~5 g were mixed to produce LaB_6 – BaB_6 in 50:50 or 40:60 (La:Ba) molar proportions as given by Eqs. (1) and (2) respectively.



Three basic variations of the method were used. In method A, the effects of sintering time at a temperature of 1400 °C were evaluated. The starting materials were milled for 20 min using zirconia media in a SPEX8000 mixer mill with a ball-to-powder ratio of 5:1. This corresponds to the lower end of the high-energy milling range. Milled powders were pressed into 19 mm diameter pellets for firing in a moderate vacuum under conditions set out in Table 1.

In method B the effects of pre-milling the starting oxide and carbonate (La_2O_3 and BaCO_3) were investigated. The oxide/carbonate reactants were pre-milled in order to begin solid solution formation in the precursor material. Following this pre-milling, B_4C and C were added and a further milling period was conducted. Subsequently, pellets were pressed and fired under the conditions shown in Table 1.

In method C, the effects of secondary high temperature treatment was evaluated. The pre-fired pellets prepared using method B were ground, milled for 1 h, pressed and re-fired at 1950 °C for 1 h using a high-vacuum tantalum furnace. Characterisation was carried out on both pellets and crushed powders. Prior to characterisation, all pellet samples were abraded by 0.2–0.5 mm to remove any possible surface contaminants due to the prevailing conditions in the furnace.

The phases present in the mixed borides were analysed by X-ray diffraction (Philips 1710 and Analytical X'pert MPD) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$), operating at an accelerating voltage of 40 kV, an emission current of 40 mA and a scanning rate of $0.025^\circ/\text{s}$ over the 2θ range 20–80°. Phase identification utilised the International Centre for Diffraction Data (ICDD) database. Standard structural

Table 1
Material preparation conditions.

Material	Ba:La ratio	Method	Sintering T (°C)	Sintering time (h)	Milling time
1	1:1	A	1400	2	20 min
2	1:1	A	1400	4	20 min
3	1:1	A	1400	14	20 min
4	6:4	B	1400	4	Pre-mill 1 h, co-mill 20 min
5	6:4	B	1400	4	Pre-mill 24 h, co-mill 20 min
6	6:4	A	1500	2	20 min
7	6:4	B	1500	2	Pre-mill 4 h, co-mill 20 min
8	6:4	C	1950	1	Sample 7 re-milled 1 h

Table 2
Standard structural models of BaB_6 , LaB_6 and $(\text{La}_x\text{Ba}_{1-x})\text{B}_6$.

	BaB_6	LaB_6	$(\text{La}_x\text{Ba}_{1-x})\text{B}_6$
Crystal system	Cubic	Cubic	Cubic
Space group	$\text{Pm}\bar{3}\text{m}$	$\text{Pm}\bar{3}\text{m}$	$\text{Pm}\bar{3}\text{m}$
Lattice parameters, a (Å)	4.2615	4.1570	4.2000
Boron position	$x = 0.5, y = 0.5, z = 0.2054$	$x = 0.5, y = 0.5, z = 0.1975$	$x = 0.5, y = 0.5, z = 0.202$

models of BaB_6 , LaB_6 and $\text{La}_{0.5}\text{Ba}_{0.5}\text{B}_6$ (seen in Table 2) were utilised to confirm the phase identification for quantitative phase analysis of all samples using Rietveld refinement and the method of Hill and Howard [12].

The surface morphology of the as-fired, abraded and post-emission pellets was characterized using secondary electron and backscattered electron imaging, and the chemical composition of samples was investigated by means of energy dispersive X-ray analysis (EDX) using a ZEISS Sigma VP FESEM equipped with a Bruker light element Silicon strip detector (SSD) and operated at accelerating voltages of 3–25 kV.

Thermionic emission to evaluate the emission constants was performed on abraded samples in a Schottky device in the temperature range of 1400–1540 K using a 3 mm gap between the emitter and the collector. The collector itself had a rectangular shape 2.5 by 4.5 mm. Vacuum was maintained at $<1 \times 10^{-3} \text{ Pa}$ during testing and prior to data collection the samples were activated for 1 h at the highest operating temperature. DC emission testing was carried out by applying accelerating voltages in the range of 0–300 V during a series of constant temperature holds. Schottky and Richardson plots were used to find the Richardson work function of the sample sintered at 1950 °C in accordance with ASTM Standard F83-71 [13].

3. Results and discussion

Materials prepared using method A with a 50:50 La:Ba compositional ratio represent a coherent set investigating the influence of sintering time on the formation of the boride solid solution. XRD patterns from these samples are shown in Fig. 1. The major peaks belong to cubic BaB_6 and LaB_6 as indicated by the arrows. The sample fired for 2 h also shows the presence of the intermediate BaB_2O_4 phase, unreacted boron carbide and BaO. The pronounced intensity saddle between the LaB_6 and BaB_6 peaks indicates that a solid solution $(\text{La}_x\text{Ba}_{1-x})\text{B}_6$ has formed in addition to the pure boride phases. There is little apparent improvement in the proportion of the boride solid solution after heating to 1400 °C for 14 h instead of 4 h or even 2 h. Therefore, whereas the individual borides were readily synthesised at this temperature, solid solution formation halted quite early in the process.

In Fig. 2, XRD patterns for materials prepared using method B and fired at 1400 °C for 4 h show that this procedure also resulted in a two boride mixture with some solid solution. The sample milled for 24 h displays some ZrB_2 as the milling was performed in a zirconia ball and vial system. It also shows a larger particle size (narrower peaks) as well as approximately the same degree of solid solution compared to those produced by method A. The relative

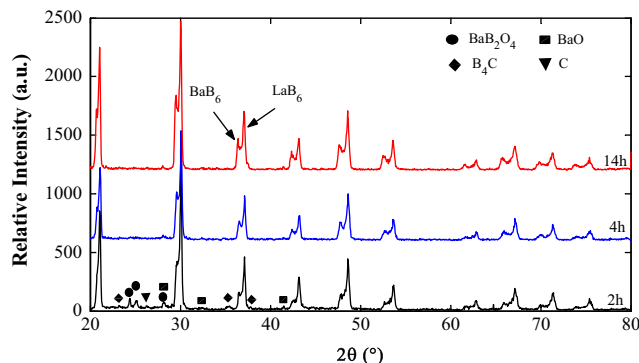


Fig. 1. Effect of time at 1400 °C on XRD patterns for LaB_6 – BaB_6 (molar ratio 50:50) produced by method A.

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