



Structural, magnetic, and thermionic emission properties of multi-functional $\text{La}_{1-x}\text{Ca}_x\text{B}_6$ hexaboride



Lihong Bao^{*}, Xiaoping Qi, Tana Bao, O. Tegus

Inner Mongolia Key Laboratory for Physics and Chemistry of Functional Materials, College of Physics and Electronic Information, Inner Mongolia Normal University, Hohhot 010022, China

ARTICLE INFO

Article history:

Received 5 March 2017

Received in revised form

8 October 2017

Accepted 9 October 2017

Available online 10 October 2017

Keywords:

Nanocrystalline

Rare-earth hexaborides

Magnetic properties

Work function

ABSTRACT

Herein, we report the synthesis of nanocrystalline $\text{La}_{1-x}\text{Ca}_x\text{B}_6$ ($0 \leq x \leq 1$) hexaboride powders by solid-state reaction and their subsequent consolidation via spark plasma sintering. The structural, magnetic and thermionic emission properties of $\text{La}_{1-x}\text{Ca}_x\text{B}_6$ hexaboride are investigated. All of the synthesized nanocrystalline hexaboride powders are single phase with the *CsCl*-type structure and no ferromagnetic impurity phases have been detected from X-ray diffraction. Magnetic measurements show that weak ferromagnetism at room temperature is found in nanocrystalline $\text{La}_{1-x}\text{Ca}_x\text{B}_6$ hexaboride powders, and the magnetism was attributed to the presence of the intrinsic defects, based on the data of the HRTEM. Thermionic emission measurements indicate that the maximum emission intensity for bulk $\text{La}_{0.4}\text{Ca}_{0.6}\text{B}_6$ at 1873 K reached 20.02 A/cm², which is more than three times higher as compared to bulk CaB_6 (~6.04 A/cm²). When the La doping was increased to 40 at%, the work function of CaB_6 decreased from 2.95 to 2.76 eV, indicating an improvement in the thermionic emission performance. Therefore, the quasibinary $\text{La}_{1-x}\text{Ca}_x\text{B}_6$ hexaboride may have an application as a promising cathode.

© 2017 Published by Elsevier B.V.

1. Introduction

Recently, nanocrystalline lanthanum hexaboride (LaB_6) was found to possess a number of attractive physical and chemical properties as compared to coarse-grained bulk samples of the same material [1–3]. One of the important findings is that nano-scale LaB_6 can be used as a low work function material in the charge collective interlayer in organic photovoltaic solar cells [4]. As a result, this material can enhance the built-in voltage, resulting in a higher fill factor (FF), which in turn can significantly improve the power conversion efficiency. In addition, nanosized LaB_6 is an efficient optical absorption material and has potential applications for improving the efficiency of organic photovoltaic cells, as they are highly transparent in the visible light spectrum [5–7]. Therefore, there are great possibilities to apply nanocrystalline LaB_6 in organic photovoltaic-devices.

In general, in order to further improve the performance of LaB_6 in terms of its electron emission capacity or optical absorption intensity, several compositional and microstructural factors should be taken into consideration. It has been reported that

doping La into PrB_6 leads to a reduction in the effective work function [8]. Moreover, multiple substituted rare-earth hexaborides exhibit a much-improved emission performance compared to pristine LaB_6 . Zhou et al. [9] reported enhanced thermionic emission from partially Ba-doped LaB_6 in bulk, polycrystalline form. Recently, after the observation of high temperature ferromagnetism in La-doped CaB_6 single crystals by Young et al. [10], such materials have attracted a great attention in the study of magnetic interactions in the absence of 3d or 4f electrons [11]. Subsequently, there have been many proposed explanations for the presence of weak ferromagnetism in CaB_6 , both experiment and theory. One suggestion is that the weak ferromagnetic properties of CaB_6 single crystals are induced by ferromagnetic impurity phases, such as iron or FeB compounds [12,13]. In contrast, other researchers have discovered a room temperature weak ferromagnetism in CaB_6 or BaB_6 thin films and related it to the crystal defects [14,15]. These opposing view-points make the hexaborides a subject deserving further study. Nevertheless, the magnetic properties of nanocrystalline La-doped CaB_6 systems have rarely been reported, in spite of their interesting magnetic properties. Consequently, further studies of this topic are one of our present research objectives. Furthermore, determining whether doping La into CaB_6 can reduce the work function of the

^{*} Corresponding author. Tel./fax: +86 4714393246.

E-mail address: baolihong@imnu.edu.cn (L. Bao).

parent compound is another purpose of the research presented here.

In the following, we report the synthesis of nanocrystalline La-doped CaB_6 powders via solid-state reaction and of bulk material with micron-sized grains via spark plasma sintering. The structural, magnetic and thermionic emission properties of the materials thus prepared have undergone systematic investigation, the results of which are reported here.

2. Experimental section

2.1. Synthesis of nanocrystalline powder and bulk materials

Lanthanum oxide (99.99% purity, Baotou rare-earth Institute), calcium oxide (99.95% purity, Aladdin) and sodium borohydride (99.0% purity, Sigma-Aldrich) powders were mixed in a stoichiometric molar ratio of $x:1-x:6$ ($x = 0-1$). Then the mixtures were pressed into the thin pellets, and placed in a resistance furnace at a reaction temperature of 1150–1200 °C for 2 h. The interacting mixture was kept under a vacuum of 2×10^{-2} bar. After the reaction, the products were washed with hydrochloric acid and distilled water several times to remove the impurity phases of $(\text{La,Ca})\text{BO}_3$.

The synthesized nanocrystalline powders were placed into a graphite die with an inner diameter of 15 mm for solid-state SPS processing using a Sumimoto SPS-3.20 MK-V sintering system. The following conditions were applied for SPS sintering: the axial mechanical pressure was 50 MPa, the heating rate was 110 °C/min, the sintering temperatures was 1500 °C, and the holding time was 5 min.

2.2. Characterization

The phase identification was performed using X-ray diffraction ($\text{Cu K}\alpha$ radiation, Philips PW1830). The 2θ scans were taken between 20° and 80° with steps of 0.05°, with 2s counting time per angular value. The nanocrystalline morphology was characterized using a field-emission scanning electron microscope (FESEM: Hitachi SU-8010), and the microstructure was characterized using a transmission electron microscope (TEM: FEI-Tecna F20 S-Twin 200 KV). The magnetic properties of nanocrystalline hexaborides were measured using a SQUID magnetometer (Quantum Design MPMS, 7 T). For the bulk samples, electron backscattered diffraction (EBSD) measurements were carried out in an FEINANO 200 scanning electron microscope incorporating an EDAX TSL OIM5.2 system. Testing of the thermionic emission properties was carried out using home-made set-up at the University of Electronic Science and Technology of China. The emission area of the cathode was 1 mm². The emission current densities were investigated at cathode temperatures of 1673 K, 1773 K and 1873 K under a vacuum of 7×10^{-4} Pa. The cathode temperatures were measured using an optical microprometer.

3. Results and discussion

3.1. Crystal structure, morphology and microstructure of nanocrystalline $\text{La}_{1-x}\text{Ca}_x\text{B}_6$

Fig. 1 shows the XRD patterns of nanocrystalline $\text{La}_{1-x}\text{Ca}_x\text{B}_6$ hexaboride powders with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1 prepared at 1150 °C for 2 h. It can be seen that the crystal structure of the synthesized hexaborides with various Ca doping values can be indexed using the CsCl-type cubic structure with a space group of

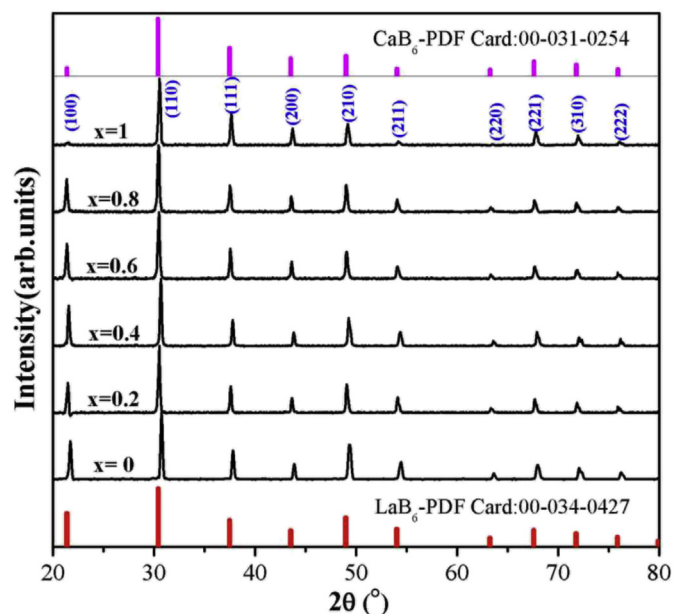


Fig. 1. XRD patterns of nanocrystalline $\text{La}_{1-x}\text{Ca}_x\text{B}_6$ powders prepared at 1150 °C.

$Pm-3m$ (PDF cards: 00-034-0427 and 00-031-0254). The diffraction peaks are well indexed and assigned to the parallel crystal planes of (100), (110), (111), (210), (211), (220), (310) and (311). We can see from Fig. 1 that the (100) and (210) peak intensities of CaB_6 are lower than those of LaB_6 . The main reason for this is that the Ca atoms have a lower scattering ability of X-Rays as compared to the La atoms, which causes the lower diffraction intensity of the (100) and (210) peaks. Furthermore, we do not find any extra impurity phases such as La_2O_3 , CaO, or $(\text{La,Ca})\text{BO}_3$, confirming the high purity of the reaction products. Moreover, we do not observe a coexistence of the two isostructural phases of LaB_6 and CaB_6 , indicating that Ca atoms randomly occupy the lattice sites of La atoms.

Fig. 2 shows typical FE-SEM images of nanocrystalline $\text{La}_{1-x}\text{Ca}_x\text{B}_6$ hexaboride powders prepared at various reaction temperatures. It can be seen from Fig. 2(a)–(d) that when the reaction temperature is 1150 °C, all of the synthesized hexaborides are primarily composed of nanocubes with mean sizes of 50 nm, in addition to small number of larger cubic crystals. When the reaction temperature is increased to 1200 °C, it can be seen in Fig. 2 (e)–(h) that the grain sizes obviously increase to 150 nm, and the grain morphology showed a higher tendency towards a perfect cubic shape. According to our previous investigations [16,17], non-cubic nanoparticles are initially formed at a reaction temperature of 1000 °C. When the reaction temperature is further increased to 1200 °C, the nanoparticles aggregated together and crystallized into perfect cubic crystals through the increased diffusion of ions or atoms. At the same time, grain growth is observed, as shown in Fig. 2 (e)–(h). However, we note that it is difficult to obtain homogenous cubic nanocrystalline powder by solid-state reaction, which leads to the observation of non-cubic morphologies of hexaboride powders.

Elemental mapping is an effective method to distinguish the mixture of phases present in a selected microscopic zone. To clarify whether individual LaB_6 or CaB_6 crystals were formed during the solid-state reaction, the nanocrystalline powders of $\text{La}_{0.2}\text{Ca}_{0.8}\text{B}_6$ as an example were used for analysis of the elemental distribution

Download English Version:

<https://daneshyari.com/en/article/5458043>

Download Persian Version:

<https://daneshyari.com/article/5458043>

[Daneshyari.com](https://daneshyari.com)