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## Structural, magnetic, and thermionic emission properties of multi-functional La<sub>1-x</sub>Ca<sub>x</sub>B<sub>6</sub> hexaboride



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#### ABSTRACT

Herein, we report the synthesis of nanocrystalline  $La_{1-x}Ca_xB_6$  ( $0 \le x \le 1$ ) hexaboride powders by solidstate reaction and their subsequent consolidation via spark plasma sintering. The structural, magnetic and thermionic emission properties of  $La_{1-x}Ca_xB_6$  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  $La_{1-x}Ca_xB_6$  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  $La_{0.4}Ca_{0.6}B_6$ at 1873 K reached 20.02 A/cm<sup>2</sup>, which is more than three times higher as compared to bulk CaB<sub>6</sub> (~6.04 A/cm<sup>2</sup>). When the La doping was increased to 40 at%, the work function of CaB<sub>6</sub> decreased from 2.95 to 2.76 eV, indicating an improvement in the thermionic emission performance. Therefore, the quasibinary  $La_{1-x}Ca_xB_6$  hexaboride may have an application as a promising cathode.

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#### 1. Introduction

Recently, nanocrystalline lanthanum hexaboride (LaB<sub>6</sub>) 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<sub>6</sub> 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<sub>6</sub> 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<sub>6</sub> 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<sub>6</sub> 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<sub>6</sub>. Zhou et al. [9] reported enhanced thermionic emission from partially Ba-doped LaB<sub>6</sub> in bulk, polycrystalline form. Recently, after the observation of high temperature ferromagnetism in La-doped CaB<sub>6</sub> 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<sub>6</sub>, both experiment and theory. One suggestion is that the weak ferromagnetic properties of CaB<sub>6</sub> 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<sub>6</sub> or BaB<sub>6</sub> 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<sub>6</sub> 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<sub>6</sub> can reduce the work function of the

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parent compound is another purpose of the research presented here.

In the following, we report the synthesis of nanocrystalline Ladoped  $CaB_6$  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  $2 \times 10^{-2}$  bar. After the reaction, the products were washed with hydrochloric acid and distilled water several times to remove the impurity phases of (La,Ca)BO<sub>3</sub>.

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 (Cu K<sub> $\alpha$ </sub> radiation, Philips PW1830). The 2 $\theta$  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-Tecnai 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  $1 \text{ mm}^2$ . The emission current densities were investigated at cathode temperatures of 1673 K, 1773 K and 1873 K under a vacuum of  $7\,\times\,10^{-4}$  Pa. The cathode temperatures were measured using an optical micropyrometer.

#### 3. Results and discussion

### 3.1. Crystal structure, morphology and microstructure of nanocrystalline $La_{1-x}Ca_xB_6$

Fig. 1 shows the XRD patterns of nanocrystalline  $La_{1-x}Ca_xB_6$  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  $La_{1-x}Ca_xB_6$  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<sub>6</sub> are lower than those of LaB<sub>6</sub>. 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<sub>2</sub>O<sub>3</sub>, CaO, or (La,Ca)BO<sub>3</sub>, confirming the high purity of the reaction products. Moreover, we do not observe a coexistence of the two isostructural phases of LaB<sub>6</sub> and CaB<sub>6</sub>, indicating that Ca atoms randomly occupy the lattice sites of La atoms.

Fig. 2 shows typical FE-SEM images of nanocrystalline La<sub>1-</sub> <sub>x</sub>Ca<sub>x</sub>B<sub>6</sub> 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<sub>6</sub> or CaB<sub>6</sub> crystals were formed during the solid-state reaction, the nanocrystalline powders of La<sub>0.2</sub>Ca<sub>0.8</sub>B<sub>6</sub> as an example were used for analysis of the elemental distribution



**Fig. 2.** (a)-(d) FESEM images of nanocrystalline La<sub>1-x</sub>Ca<sub>x</sub>B<sub>6</sub> (x = 0, 0.2, 0.4, 0.8) powders prepared at 1150 °C. Fig. 2 (e)-(h) La<sub>1-x</sub>Ca<sub>x</sub>B<sub>6</sub> (x = 0, 0.2, 0.4, 0.8) powders prepared at 1200 °C. The lower image corresponds to the energy mapping results of La<sub>0-2</sub>Ca<sub>0.8</sub>B<sub>6</sub> prepared at 1200 °C.

(see the lowest part of Fig. 2). The La, Ca, and B elements are distributed homogeneously in the selected zone indicating the formation of a single phase. As observed from the elemental analysis, no ferromagnetic impurity element could be found. As for the presence of other impurity elements, it is possible that oxygen and chlorine are introduced at the sample surface during the hydrochloric acid washing, silicon maybe introduced by diffusion from the quartz tube at high reaction temperatures used, and the aluminum signal comes primarily from the conductive adhesive. Limitations in the resolution of the SEM meant an EDS analysis of a single nanocrystal was not possible using this technique. Therefore, the microstructure and detailed compositional information for single nanocrystals of La<sub>0.4</sub>Ca<sub>0.6</sub>B<sub>6</sub> was investigated using a transmission electron microscope. It can be seen from Fig. 3 (a) that this crystal has a cubic-shaped morphology with an average grain size of 50 nm. Fig. 3 (b)-(e) displays the corresponding HAADF-STEM images and elemental mapping results. The La, Ca and B elements are uniformly distributed in this single crystal, which indicates that the Ca element has been successfully doped into the lattice of LaB<sub>6</sub>. The EDS analysis of shown in Fig. 3(f), does not show the presence of ferromagnetic impurity phases in the selected single crystal, which is consistent with the SEM results.

#### 3.2. Crystallographic orientation of bulk samples

Bulk La<sub>1-x</sub>Ca<sub>x</sub>B<sub>6</sub> samples with grain sizes on the micron scale were prepared by the spark plasma sintering (SPS) method in an oxygen-free system. By comparison with hot-pressing sintering, this technique is a promising method to not only densify the ceramic powders rapidly, but also prepare grain-orientated bulk samples because of the special sintering mechanism [18]. Fig. 4 shows the EBSD pole figures and inverse pole figures for polished bulk samples of CaB<sub>6</sub> and La<sub>0.6</sub>Ca<sub>0.4</sub>B<sub>6</sub>, where the color depth indicates the pole area density. It can be seen from Fig. 4 (a) and (b) that both samples are characterized by the preferred orientation of the {111}<-6,-34,31>, {111}<-12,-33,14>, and {111}<-2,34,37> directions, which are marked by numbers and boxes. From the inverse pole figures of Fig. 4(c) and (d), both bulk samples displayed a strong (111) texture. According to the earlier investigations [19], the work functions ( $\Phi$ ) of hexaboride materials depend on the surface orientation, whereby the (111) crystal surface should have a lower work function than the others. Thus, we predict that the bulk La<sub>1-</sub> <sub>x</sub>Ca<sub>x</sub>B<sub>6</sub> samples with (111) texture should exhibit excellent emission properties.



**Fig. 3.** (a) TEM analysis of the nanocrystalline  $La_{0.4}Ca_{0.6}B_6$  prepared at 1150 °C, (b) the HAADF–STEM analysis, (c)-(e) La, Ca and B elements mapping, (f) elemental spectra.

#### 3.3. Magnetic properties

Fig. 5(a) shows the room-temperature magnetization characteristics of nanocrystalline  $La_{1-x}Ca_xB_6$  (x = 0.2, 0.4, 0.6, 1) hexaboride powders with a maximum magnetic field of 5 T after subtracting the diamagnetic background of the tetrafluoroethylene capsule, where a 10-mg sample is used for every magnetic measurement. It is interesting to note that at the initial low magnetic field, the magnetic moments of all hexaboride samples show an abrupt increase and reach saturation magnetizations  $(M_s)$  of  $2.12\times10^{-8}$  Am²,  $1.28\times10^{-8}$  Am²,  $1.8\times10^{-8}$  Am² and  $3.24\times10^{-8}$ Am<sup>2</sup>, respectively, exhibiting a room-temperature weak ferromagnetism. According to Sakuraba et al. [20], Ackland et al. [21,22] and Liu et al. [23], room-temperature weak ferromagnetism was also found in La-doped CaB<sub>6</sub> or BaB<sub>6</sub> thin film materials, which is very similar to the present work. Thus, to clarify the mechanism of the room-temperature weak ferromagnetism of nanocrystalline  $La_{1-x}Ca_{x}B_{6}$ , we initially studied whether the ferromagnetic impurity phase contributes to the magnetism. However, we did not find any ferromagnetic impurity phase from the XRD analysis or EDS analysis with SEM and TEM. Subsequently, we attempted to calculate the magnetic moments of La1-xCaxB6 hexaboride theoretically using the DFT method. The nominal composition of a  $La_{0.625}Ca_{0.375}B_6$  crystal with 2  $\times$  2  $\times$  2 supercells was selected, and calculation results are shown in Fig. 5(b), where the green dotted line is taken from Ref. [17] for comparison. It can be seen from the calculation results that the high symmetry of spin up and spin down total density of states indicate the zero local magnetic moments for La<sub>0.625</sub>Ca<sub>0.375</sub>B<sub>6</sub>.



Fig. 4. (a) and (b) pole figures, (c) and (d) ND inverse pole figures for  $CaB_6$  and  $La_{0.6}Ca_{0.4}B_6$  bulks.

Based on the above mentioned analysis, it can be inferred that the weak ferromagnetism of nanocrystalline La1-xCaxB6 powders should originate from the intrinsic defects. Cao et al. [24] have calculated the magnetic moments of CaB6 with the local lattice distortion induced by moving a boron cage. As a result, the B atoms in this distorted system have a negative charge and provide 1/3 of an extra electron, resulting in ferromagnetism. For non-magnetic system such as ZnO or CuO [25,26], the atomic vacancies or crystal defects are also related to the ferromagnetism. Therefore, to better identify the crystal defects, a high resolution transmission electron microscopy (HRTEM) was used to assess the crystal defects in nanocrystalline La0.4Ca0.6B6 hexaboride. It can be seen from Fig. 6 that the lattice fringes of d = 0.42 nm agree well with the (100) crystal plane, and some fuzzy regions marked by yellow boxes indicate the evidence of crystal defects. To further clarify the intrinsic defects at various crystal surfaces, Fig. 7 (b) and (d) show the inverse FFT patterns along the (100) crystal plane, which is transformed from the FFT patterns of Fig. 7(a) and (c) and correspond to the marked zones of Fig. 6 (a) and (b). It can be clearly seen from Fig. 7 (b) and (d) that there are many edge dislocations and lattice distortions. Meanwhile, we can directly see the obvious edge dislocation from the locally enlarged image of Fig. 7 (e), which is denoted by the symbol "T". This kind of dislocation is often related to the lattice distortion proceeding in a thin layer containing 1-2atomic planes. Therefore, we excluded the possibility of a ferromagnetic impurity phase contributing to the room-temperature weak ferromagnetism and assume that it originates from the intrinsic defects. As for the formation of crystal defects, it maybe due to the different values of ionic radii of Ca2+(~1.0 Å) and La3+(~1.18 Å), which can lead to the crystal defects. Another possibility is that the evaporation of Ca element also leads to edge dislocation during the high temperature synthesis procedure. The higher magnetization of CaB6 shown in Fig. 5(a), maybe associated with the crystal's intrinsic defects. During the sample preparation procedure, we find that the CaO starting material evaporates more readily than La2O3 at the same reaction temperature, which indicates that using the same chemical ratio of oxide to sodium borohydride (1:6) it will not be possible to prepare a phase-pure



Fig. 5. (a) Room-temperature magnetization curves for nanocrystalline  $La_{1-x}Ca_xB_6$  powders prepared at 1150 °C (b) calculated partial density of states (PDOS) for  $La_{0.625}Ca_{0.375}B_6$  and  $La_{0.625}Ba_{0.375}B_6$ .

nanocrystalline CaB6 powder, and more CaO must be added. This means that when the La3+ ion occupies the lattice site of Ca2+, it should give a rise to fewer intrinsic defects and smaller magnetization.

#### 3.4. Thermionic emission of bulk samples

In general, CaB<sub>6</sub> has been extensively studied as a neutronabsorbing material, a deoxidation agent, and a refractory material [27,28]. However, the thermionic emission properties have been rarely reported. In this section, we discuss the thermionic emission properties of bulk CaB<sub>6</sub> and the La doping effects at various cathode temperatures from 1673 K to 1873 K and applied voltages up to 4000 V. It can be seen from Fig. 8(a) that the maximum emission intensity for CaB<sub>6</sub> is 6.04 A/cm<sup>2</sup> at 1873 K. When the La doping is increased to 40 at%, the maximum emission intensity suddenly increased to 20.02 A/cm<sup>2</sup> at 1873 K, as shown in Fig. 8(b), which is more than three times higher as compared to bulk CaB<sub>6</sub> (~6.04 A/ cm<sup>2</sup>), but is still lower than that of pure LaB<sub>6</sub> (~36.2 A/cm<sup>2</sup> [29]). With further increasing of the La doping to 60 at% and 80 at%, the emission intensity for La<sub>0.6</sub>Ca<sub>0.4</sub>B<sub>6</sub> and La<sub>0.8</sub>Ca<sub>0.2</sub>B<sub>6</sub> did not increase, and their maximum values were 5.91 A/cm<sup>2</sup> and 5.37 A/cm<sup>2</sup> at 1873 K, respectively. This implies that a La doping of 40 at% can reduce the work function of CaB<sub>6</sub> effectively.

To further characterize the electron emission ability, the effective work function ( $\Phi_e$ ) was calculated using the Richardson-Dushman formula  $\Phi_e = KT \ln(AT^2|J_0)$ , where *K* is a Bolzmann's constant, *T* is the cathode temperature, *A* is the theoretical Richardson constant of  $A = 120 \text{ Acm}^{-2}\text{K}^{-2}$ , and  $J_0$  is the zero-field emission density obtained by the square root of the applied voltage with the logarithm value of the emission density. Fig. 9 shows the Schottky plots for bulk CaB<sub>6</sub> and La<sub>0.4</sub>Ca<sub>0.6</sub>B<sub>6</sub> using the experimental data of applied voltages and emission current density measured at 1873 K. It is observed that the  $J_0$  values of CaB<sub>6</sub> and



Fig. 6. (a) and (b) HRTEM analysis of nanocrystalline La<sub>0.4</sub>Ca<sub>0.6</sub>B<sub>6</sub>.



**Fig. 7.** (a) and (c) Fast Fourier transformed (FFT) patterns, (b) and (d) inverse FFT patterns corresponding to the yellow dashed zone of Fig. 6 (a) and (b), Fig. 7(e) High resolution TEM image of crystal defects. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

 $La_{0.4}Ca_{0.6}B_6$  are 5.01 Acm<sup>-2</sup> and 15.85 Acm<sup>-2</sup> respectively. Their corresponding effective work functions are 2.95 eV and 2.76 eV, which means that the work function of CaB<sub>6</sub> is effectively reduced by the La-doping method. Thus, multiple  $La_{0.4}Ca_{0.6}B_6$  hexaboride as low-work function ceramics should allow a multifunctional usage as promising thermionic emission cathodes or a charge collective interlayer in organic photovoltaic solar cells.

#### 4. Conclusions

In summary, the structural, magnetic and thermionic emissions properties of multifunctional  $La_{1-x}Ca_xB_6$  hexaborides were investigated. XRD, SEM and TEM data were used to characterize the crystal structure, grain morphology, and crystal defects,

respectively. The magnetic measurement results show that roomtemperature weak ferromagnetism was observed for nanocrystalline La<sub>1-x</sub>Ca<sub>x</sub>B<sub>6</sub> hexaboride powders, with the ferromagnetic properties caused by the intrinsic defects, a conclusion based on data from HRTEM studies. Furthermore, bulk La<sub>1-x</sub>Ca<sub>x</sub>B<sub>6</sub> displayed excellent thermionic emission properties at 1873 K. The maximum emission intensity for bulk La<sub>0.4</sub>Ca<sub>0.6</sub>B<sub>6</sub> reached 20.02 A/cm<sup>2</sup>, which is more than three times higher as compared to bulk CaB<sub>6</sub> (~6.04 A/ cm<sup>2</sup>). When the La doping increased to 40 at%, the work function of CaB<sub>6</sub> decreased from 2.95 eV to 2.76 eV, indicating an improvement in the thermionic emission performance. Therefore, the quasibinary La<sub>1-x</sub>Ca<sub>x</sub>B<sub>6</sub> hexaborides may find an application as a promising cathode.



Fig. 8. Thermionic emission current density of La<sub>1-x</sub>Ca<sub>x</sub>B<sub>6</sub> bulks prepared by SPS.



Fig. 9. Typical Schottky plots for CaB<sub>6</sub> and La<sub>0.4</sub>Ca<sub>0.6</sub>B<sub>6</sub> bulks at 1873 K.

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