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A low-temperature route for the synthesis of nanocrystalline LaB_6

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Abstract

Nanocrystalline lanthanum hexaboride (LaB_6) with mean particle size of 30 nm has been successfully synthesized at 400 °C in an autoclave starting from metallic magnesium powder, $NaBH_4$ and $LaCl_3$. In this case, by using B_2O_3 instead of $NaBH_4$, LaB_6 nanocubes with mean size of ~200 nm were formed at 500 °C. The X-ray diffraction (XRD) pattern can be indexed as cubic LaB_6 with the lattice constant of $a = 4.151$ Å for LaB_6 nanoparticles and 4.154 Å for LaB_6 nanocubes. An atomic ratio of La and B as 1:5.94 was determined from EDS for LaB_6 nanoparticles. XPS data of LaB_6 nanocubes indicate the atomic ratio of La to B as 1:5.95. Raman spectra indicate the formation of LaB_6.

Keywords: LaB_6; Nanoparticles; Nanocubes; Low temperature; Synthesis

1. Introduction

Lanthanum hexaboride (LaB_6) is a refractory compound characterized by a high melting temperature, excellent thermal stability, high hardness, and has found application as one of the most widely used thermionic electron sources in a large variety of devices requiring electron emission which can offer high brightness and long service life, because of its low work function (~2.6 eV) [1,2], high current and voltage capability, and low vapor pressure at high temperature [3].

Usually, LaB_6 is prepared by high-temperature reaction, such as the direct solid-phase reaction of lanthanum or its oxides with elemental boron around 1800 °C [4–7], the floating zone method of rare-earth oxides with boron at 1700 °C [8], carbothermal reduction of lanthanum oxide and boron at 1500 °C [9], the aluminum flux using $LaCl_3$ and B_2O_3 as precursors around 1500 °C [10], chemical vapor deposition (CVD) method using $LaCl_3$ powders and BCl_3 gas in an atmosphere of hydrogen and nitrogen at 1150 °C [11,12]. Recently, LaB_6 crystals have been synthesized from molten salt electrolysis at 850 °C [13]. Also, LaB_6 thin films were deposited by the pulsed laser deposition (PLD) technique at 850 °C [2].

In this paper, we report a convenient route to prepare LaB_6 nanoparticles at 400 °C via a solid-state reaction of metallic magnesium powder with $NaBH_4$ and $LaCl_3$ in an autoclave. In this case, LaB_6 nanocubes were prepared at 500 °C by using B_2O_3 instead of $NaBH_4$. The reactions can be described as follows:

$$LaCl_3 \cdot 7H_2O + 6NaBH_4 + 4Mg = LaB_6 + 3NaCl + 4MgO + 3NaOH + 17.5H_2 \uparrow \quad (1)$$

$$LaCl_3 \cdot 7H_2O + 3B_2O_3 + 17.5Mg = LaB_6 + 1.5MgCl_2 + 16MgO + 7H_2 \uparrow. \quad (2)$$

2. Experimental

2.1. Sample preparation

2.1.1. Preparation of LaB_6 nanoparticles

In a typical procedure, appropriate amounts of $LaCl_3 \cdot 7H_2O$ (1.114 g), excessive $NaBH_4$ (1.000 g), and excessive

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Mg (0.800 g) were put into a stainless steel autoclave of 25 ml capacity. Then, the autoclave was sealed under Ar atmosphere and maintained at 400 °C for 4 h, followed by naturally cooling to room temperature. The products were washed with distilled water and dilute hydrochloric acid, respectively, to remove Na, NaCl, MgO and other impurities. The final products were vacuum-dried at 60 °C for 4 h. Purple powders were obtained.

2.1.2. Preparation of LaB_6 nanocubes

In a typical procedure, appropriate amounts of $LaCl_3 \cdot 7H_2O$ (0.003 mol), B_2O_3 (0.009 mol), and excessive Mg (0.075 mol) were put into a stainless steel autoclave of 25 ml capacity. Then, the autoclave was sealed under Ar atmosphere and maintained at 500 °C for 4 h, followed by naturally cooling to room temperature. The product was washed with dilute hydrochloric acid and distilled water, respectively, to remove MgO, $MgCl_2$ and other impurities. The final products were vacuum-dried at 60 °C for 4 h. Purple powders were obtained.

2.2. Sample characterization

The phase and composition of the products were determined by a Rigaku D/Max-γA rotating-anode X-ray diffractometer equipped with monochromatic high-intensity Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB MKII X-ray photoelectron spectrometer using non-monochromatized Mg$K\alpha$ X-rays as the excitation source. The morphologies of the samples were observed with a transmission electron microscope (TEM; JEOL-2010) with an attached EDS (energy-dispersive X-ray spectrum) system having an accelerating voltage of 200 kV with a tungsten filament. FESEM images were taken on a JEOL JSM-6300F SEM. Raman spectra were measured on a LABRAM-HR Raman spectrophotometer. The 514.5-nm laser was used as an excitation light source.

3. Results and discussion

The lattice parameters and the phase purity of the materials were determined by X-ray diffraction (XRD). Typical XRD patterns of the as-prepared LaB_6 nanoparticles and nanocubes are presented in Figs. 1 and 2, respectively. All the reflection peaks of the products can be easily indexed as cubic crystal system (space group: $pm3m$ (221)) of LaB_6 with a calculated lattice constant $a = 4.151 \pm 0.001$ Å for LaB_6 nanoparticles and 4.154 ± 0.001 Å for LaB_6 nanocubes, which is in good agreement with the literature value of $a = 4.153$ Å and 4.156 (JCPDS Card No: 06-0401, 34-0427). No other impurity peaks were detected.

EDS analysis of LaB_6 nanoparticles, shown in Fig. 3, reveals the presence of La and B with an atomic ratio of $1:5.94 \pm 0.03$. Fig. 4 gives the XPS spectra of the as-prepared LaB_6 nanocubes. The B 1s and La 3d core-level

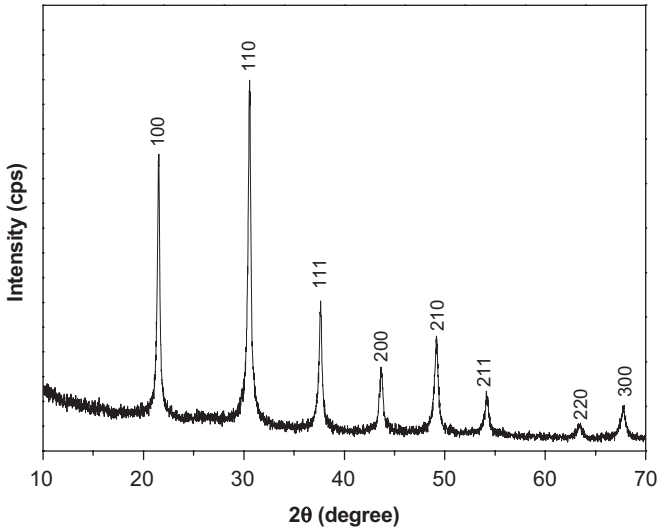

Fig. 1. XRD pattern of the LaB_6 nanoparticles.

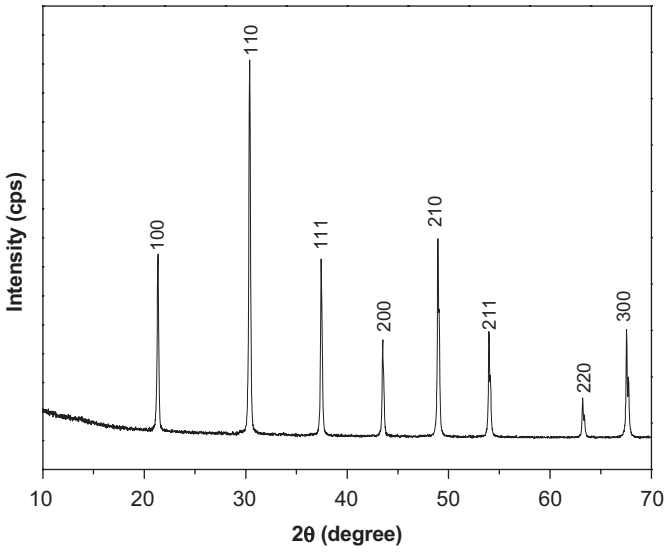

Fig. 2. XRD pattern of the LaB_6 nanocubes.

regions were examined. The binding energy of B 1s is found at 186.7 eV and that of La 3d at 836.8 and 853.1 eV. This corresponds well with the reported binding energies for LaB_6, confirming the formation of LaB_6. Based on the calculation of the peak areas, the mole ratio of La/B was obtained to be $1:5.95 \pm 0.02$, which is close to the chemical stoichiometry of LaB_6. Small amounts of nitrogen, oxygen and carbon were also detected form the XPS spectra, which may be due to the absorption of nitrogen, oxygen and carbon on the powder surface.

Fig. 5a shows the TEM image of the LaB_6 nanoparticles. It can be seen that LaB_6 crystallites are nanoparticles with mean grain size of ~30 nm, which corresponds to the calculated average result from the Scherrer equation. Fig. 5b shows the SAED pattern of LaB_6, which is consistent with the high crystallinity of the sample and reveals three clear diffraction rings in accordance with the

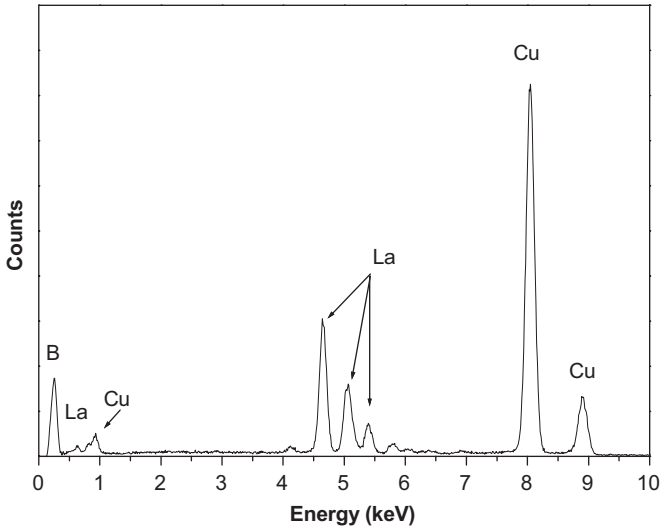

Fig. 3. EDS analysis of the LaB_6 nanoparticles, showing the presence of La and B.

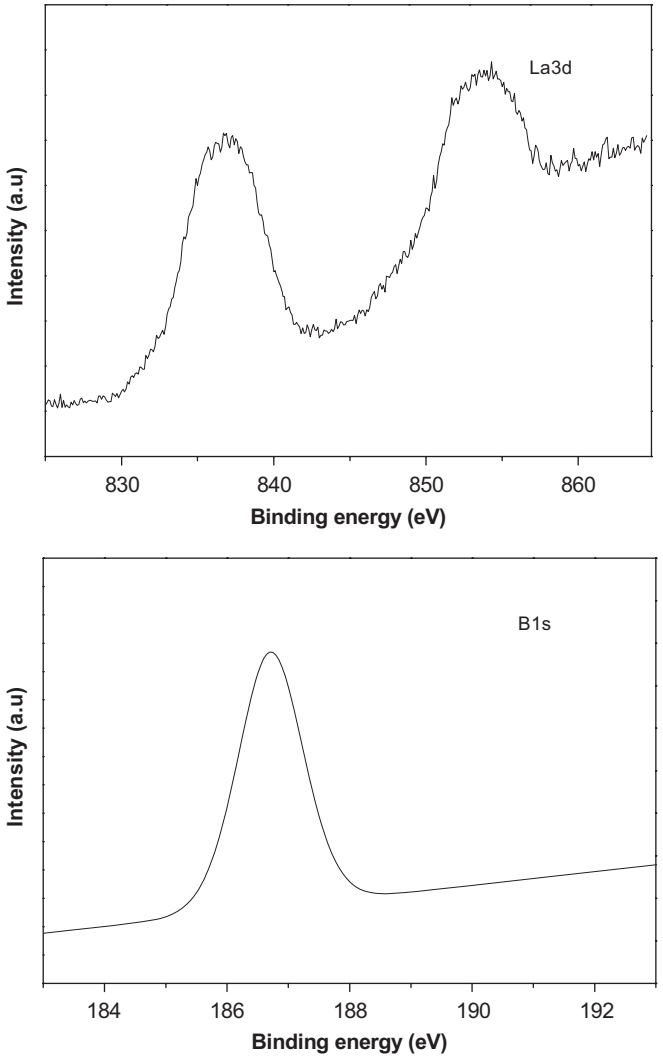

Fig. 4. XPS spectra of the LaB_6 nanocubes.

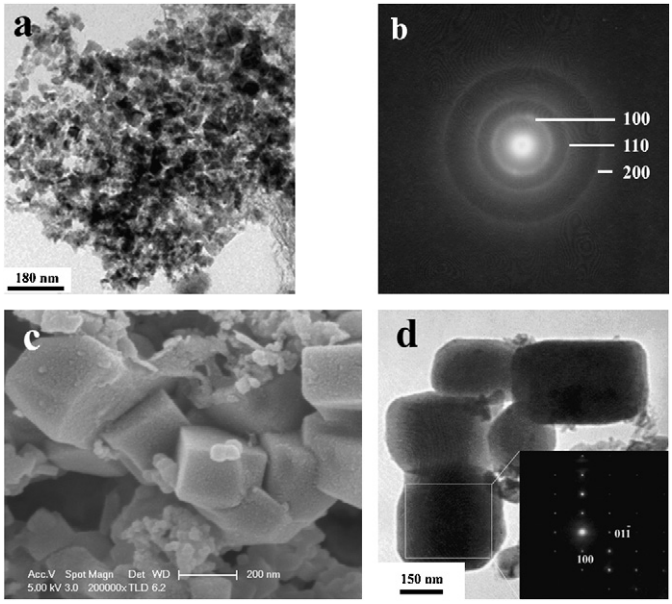

Fig. 5. (a) TEM image and (b) SAED pattern of the LaB_6 nanoparticles, (c) FESEM image of the LaB_6 nanocubes and (d) TEM image and SAED pattern of the LaB_6 nanocubes.

(100), (110), (200) crystal planes of cubic LaB_6. Fig. 5c shows FESEM image of the LaB_6 nanocubes. As can be seen, LaB_6 crystallites are nanocubes with average particle size of ~200 nm, which corresponds to the calculated average result from the Scherrer equation. A low-magnification TEM image and SAED pattern of the LaB_6 nanocubes are shown in Fig. 5d. The SAED pattern of the edge of the selected area taken along the $\langle 011 \rangle$ zone axis indicates the single-crystalline nature of individual LaB_6 nanocube.

Figs. 6 and 7 show the Raman spectra of the LaB_6 nanoparticles and nanocubes at room temperature. The three expected main peaks were observed around 680 (T_{2g}), 1120 (E_g) and 1250 (A_{1g}) cm^{-1}, which are in agreement with earlier reports [14–16], and they completely satisfy the polarization selection rule in the cubic symmetry. Other two bands around 200 and 1130 cm^{-1} are characteristic of LaB_6 sample, as observed in the literature [17]. A broad peak around 1400 cm^{-1}, labeled as "■", is commonly observed with a relatively strong intensity for trivalent and intermediate-valent crystals [18]. The above Raman spectra both indicate the formation of LaB_6.

In the present preparation process, it is found that the reaction temperature and time play important roles in the formation of LaB_6. For LaB_6 nanoparticles, no LaB_6 could be obtained if the temperature is below 350 °C. An optimum reaction temperature for LaB_6 is about 400 °C. And for LaB_6 nanocubes, the optimum reaction temperature is about 500 °C. No LaB_6 could be prepared if the temperature is below 400 °C. A series of detailed temperature-dependent experiments reveal that further increase of the reaction temperature over their optimum reaction temperature resulted in an increase of the particle size.

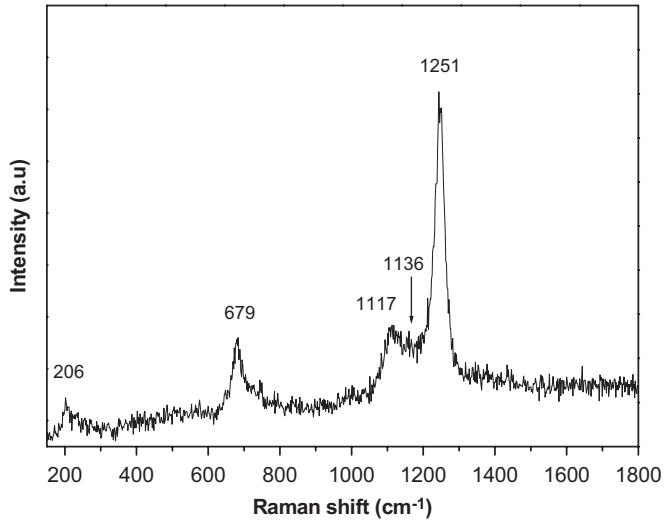

Fig. 6. Raman spectra of the LaB_6 nanoparticles at room temperature.

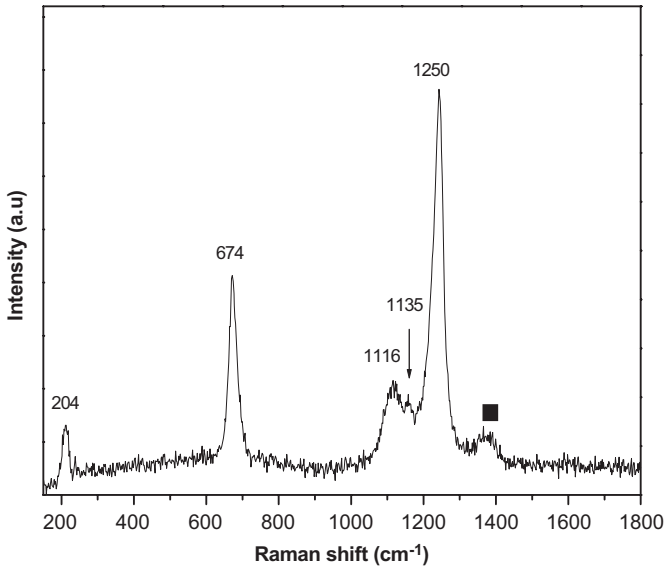

Fig. 7. Raman spectra of the LaB_6 nanocubes at room temperature.

Varying the reaction time between 4 and 12 h did not significantly affects the crystallinity or morphology for two kinds of nanocrystalline LaB_6. If the time was shorter than 2 h, the reaction became very incomplete and the crystallinity was very poor due to too short reaction time. It is noteworthy that one feature of this synthesis route is the high pressure in the autoclave, due to the H_2 (about 110 atm in reaction Eq. (1) and 55 atm in reaction Eq. (2) estimated by the ideal gas law) produced. The high pressure makes the crystalline LaB_6 form at a relatively low temperature.

4. Conclusions

In summary, nanocrystalline LaB_6 with mean particle size of 30 nm has been successfully synthesized at 400 °C in an autoclave starting from metallic magnesium powder, $NaBH_4$ and $LaCl_3$. In this case, by using B_2O_3 instead of $NaBH_4$, LaB_6 nanocubes with mean size of ~200 nm were formed at 500 °C. XRD pattern and Raman spectra both indicate the formation of LaB_6. An atomic ratio of B to La close to 6:1 was determined from EDS and XPS. In comparison with previous routes, the present route allows for the formation of nanocrystalline LaB_6 through a simpler process and at a much lower synthesis temperature. This method may be extended to synthesize other rare-earth metal borides.

Acknowledgments

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