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Short communication

A solid-state reaction route to prepare LaB_6 nanocrystals in vacuum

Yifei Yuan, Lin Zhang, Limei Liang, Kun He, Rui Liu, Guanghui Min *

Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Shandong University, Jinan 250061, PR China

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Abstract

LaB_6 nanoparticles were successfully synthesized at 1200 °C via a solid-state reaction. The synthesis was carried out under vacuum condition, with $LaCl_3$ and $NaBH_4$ as the reactants. XRD (X-ray diffraction) patterns indicated the formation of LaB_6. Result from FESEM (field emission scanning electron microscope) showed that the products were mostly composed of cubic particles with sizes ranging from 20 nm to 100 nm. HRTEM (high-resolution transmission electron microscope) images confirmed the formation of nanocrystalline LaB_6 with dominant (1 0 0) planes. Effects of different processing parameters during the reaction were investigated as well.

Keywords: Effect of parameter; Vacuum; LaB_6 nanoparticle; Optimized technology

1. Introduction

Lanthanum hexaboride (LaB_6) is widely used in modern technology as an excellent thermionic electron emission source in a large variety of devices requiring electron emission which offers high brightness and long service life [1]. The field emission stability from the single LaB_6 nanowire emitter has been proved better than W cold field emitters [2]. The advantages are originated from its low work function, satisfying high-temperature hardness [3] and high melting point [4]. Besides, LaB_6 nanoparticle recently proved effective on near-infrared absorption, bringing itself found application in reduction of solar heat gain [5]. Ceramics composites containing LaB_6 are concerned by more and more scientists because of their excellent properties in application [6].

LaB_6 nanomaterials were traditionally produced by various high temperature reactions. For example, Xu et al. [7] synthesized LaB_6 nanowires and nanotubes in a tube furnace using lanthanum powder and gas of boron trichloride (BCl_3) mixed with hydrogen and argon at 1070 °C. Zhang et al. [8] successfully synthesized LaB_6 nanocubes via a solid state reaction of metallic magnesium powder with $LaCl_3$ and B_2O_3 under Ar atmosphere. Zhang et al. [9] developed the method of chemical vapor deposition (CVD) to produce single-crystalline LaB_6 at 1150 °C.

In this paper, we reported a similar solid-state reaction route for synthesis of LaB_6 nanocrystals via reaction of $LaCl_3$ and $NaBH_4$, but in vacuum with no protective gas. Effects of different important processing parameters, such as reaction time, molar ratio of $LaCl_3$ to $NaBH_4$ and heat preservation time were also demonstrated.

2. Experimental procedure

Analytical reagent (AR) $LaCl_3{\cdot}nH_2O$ (n was estimated to be 1.1) and $NaBH_4$ were mixed thoroughly and put into a pure graphic crucible placed in the vacuum resistance furnace (model: SL-63-78, Shanghai Electric Machinery Group, P.R. China) [10]. Important technological parameters such as reaction temperature, molar ratio of $LaCl_3$ to $NaBH_4$ and heat preservation time were changed regularly, in order to study their effects on final products. Working vacuum degree during the reaction process was kept under 6.67×10^{-2} Pa, being controlled by a vacuum pump.

X-ray diffractometer (XRD, model: D/max-γA, Rigaku, Japan) was employed to analyze the obtained powder remaining in the graphic crucible with Cu Ka radiation ($\lambda = 0.154056$ nm). The morphology was observed via FESEM

* Corresponding author. Tel.: +86 531 88395639; fax: +86 531 88395639.
E-mail addresses: y13589117332@126.com (Y. Yuan), ghmin@sdu.edu.cn (G. Min).

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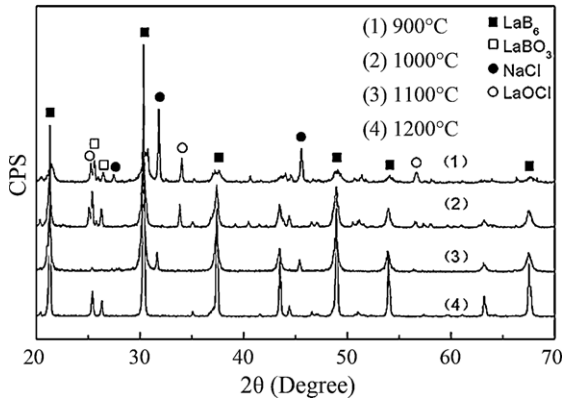

Fig. 1. XRD patterns of products produced at different temperatures, before purification. Pattern (1) 900 °C (2) 1000 °C (3) 1100 °C (4) 1200 °C.

(JEOL JSM-7600F). Based on results of XRD and FESEM, we got the optimized technology to prepare LaB_6 nanocrystals in vacuum. HRTEM images taken from a Tecnai 20U-TWIN High-Resolution TEM further confirmed the formation of LaB_6 nanomaterials.

3. Results and discussion

3.1. Effect of temperature on final products

$LaCl_3$ and $NaBH_4$ were mixed with a molar ratio of 1:6 and respectively heated to 900 °C, 1000 °C, 1100 °C and 1200 °C at a speed of 20 °C/min, then kept for 1 h in vacuum. XRD patterns of the products before purification were shown in Fig. 1. FESEM photographs of the products purified by hydrochloric acid and water were shown in Fig. 2.

From Fig. 1 we could see that reaction temperature apparently affected final products. Three kinds of impurities existed in the products gained at 900 °C: $LaBO_3$, LaOCl and NaCl. The element O might come from crystal water in $LaCl_3$. With temperature regularly increased from 900 °C to 1200 °C, most of the impurities disappeared and the height of LaB_6 peaks increased continuously, indicating less impurities and better crystallization of LaB_6 grains. Hardly any shaped nanocrystals were visible in Fig. 2a and b. Increasing reaction temperature to 1100 °C, lots of ellipsoidal and cubic nanocrystals appeared. And these particles were found to be larger and better dispersed in Fig. 2d.

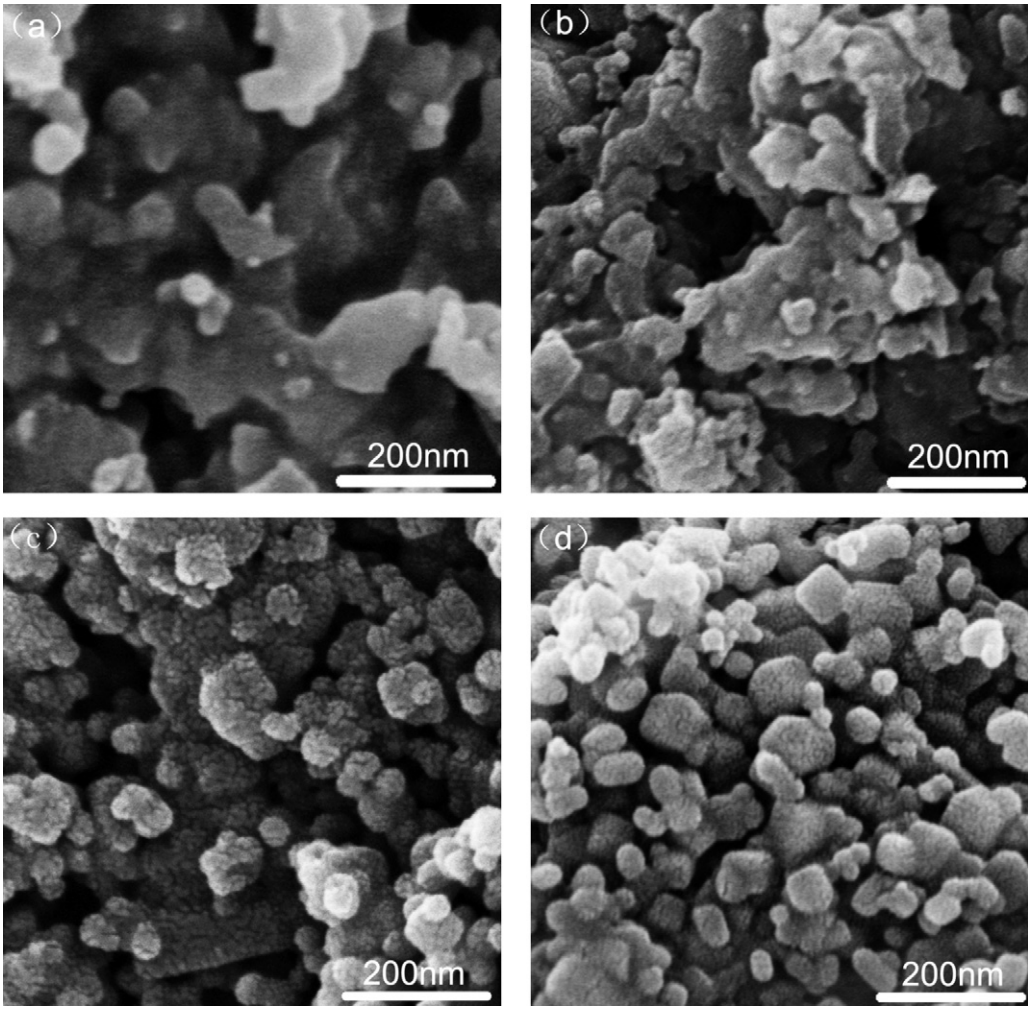

Fig. 2. FESEM images of products produced at different temperatures, purified by hydrochloric acid and water. (a) 900 °C (b) 1000 °C (c) 1100 °C (d) 1200 °C.

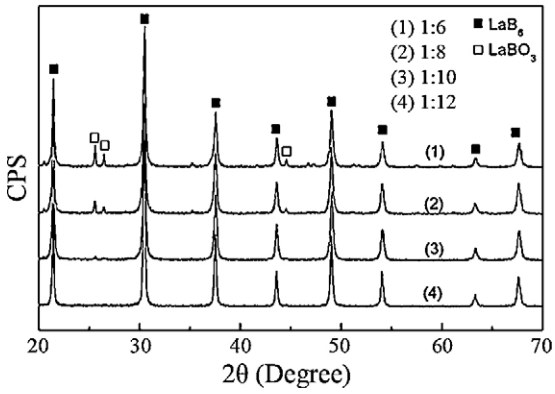

Fig. 3. XRD images of products produced with different molar ratios of $LaCl_3$ to $NaBH_4$, before purification. Pattern (1) 1:6 (2) 1:8 (3) 1::10 (4) 1:12.

It could be concluded that increasing temperature could help to form better dispersed nanocrystals with a better shape and a bigger size.

3.2. Effect of raw materials' molar ratio on final products

$LaCl_3$ and $NaBH_4$ were mixed with the molar ratio ranging from 1:6 to 1:12 and heated to 1200 °C in vacuum at a speed of 20 °C/min. XRD patterns of the products before purification were shown in Fig. 3. FESEM photographs of the products after purification by hydrochloric acid and water were shown in Fig. 4.

The main products of this group were LaB_6 and $LaBO_3$, as shown in Fig. 3. With molar ratio of 1:6, there were lots of $LaBO_3$ in the products and diffraction peaks of LaB_6 were not so significant, which indicated imperfect crystallization. With continual increase of the proportion of $NaBH_4$, $LaBO_3$ peaks

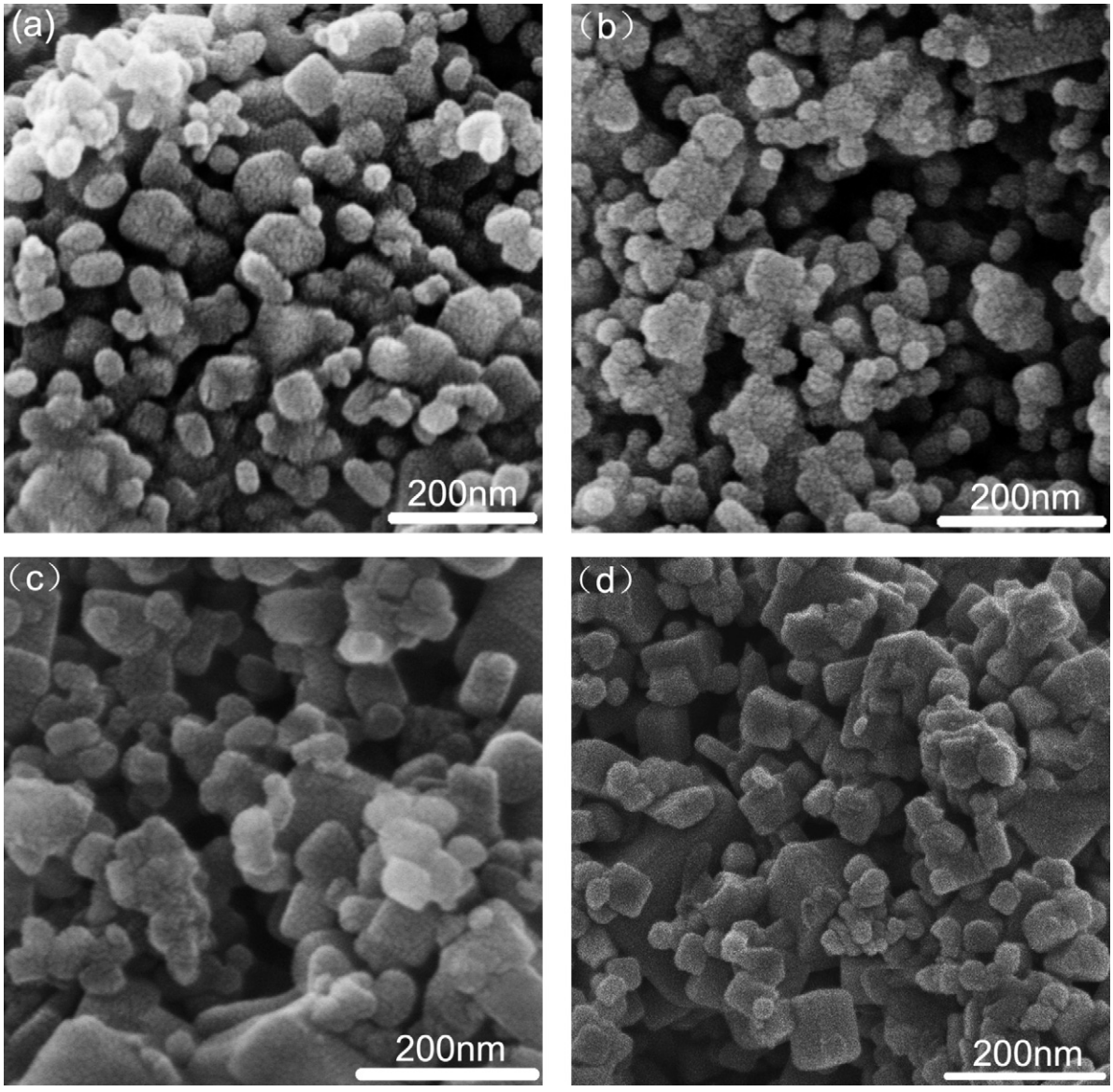

Fig. 4. FESEM images of products produced with different molar ratios of $LaCl_3$ to $NaBH_4$, purified by hydrochloric acid and water. (a) 1:6 (b) 1:8 (c) 1:10 (d) 1:12.

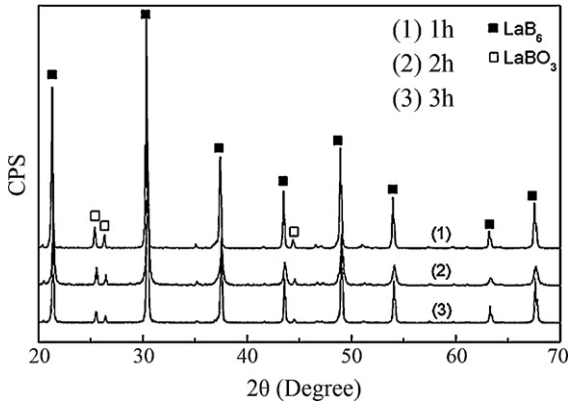

Fig. 5. XRD images of products kept at 1200 °C for different heat preservation time, before purification. Pattern (1) 1 h (2) 2 h (3)3 h.

became weaker and the peaks of LaB_6 became stronger. No evidence of $LaBO_3$ impurity was caught when the ratio was 1:12. The morphologies of particles shown via the four images in Fig. 4 were obviously different. With molar ratios of 1:6 and 1:8, most particles appeared with an ellipsoidal shape and cubic ones took a smaller portion. With the increase of $NaBH_4$, more grains with a cubic shape appeared. And when the ratio was 1:12, there were mostly cubic grains with a regular shape, indicating better crystallization.

Then we could conclude that the increase of proportion of $NaBH_4$ helped to get more LaB_6 grains with better crystallization, while the theoretical ratio value (1:6) could not lead to perfect. Reason for this lay in the decomposition of $NaBH_4$ beginning in vacuum at 400 °C [11], which temperature was not high enough to induce the reaction between $LaCl_3$ and $NaBH_4$. This resulted in the lack of $NaBH_4$ later when the temperature was suitable for formation of LaB_6 nuclei. So in order to realize complete reaction between $LaCl_3$ and $NaBH_4$,

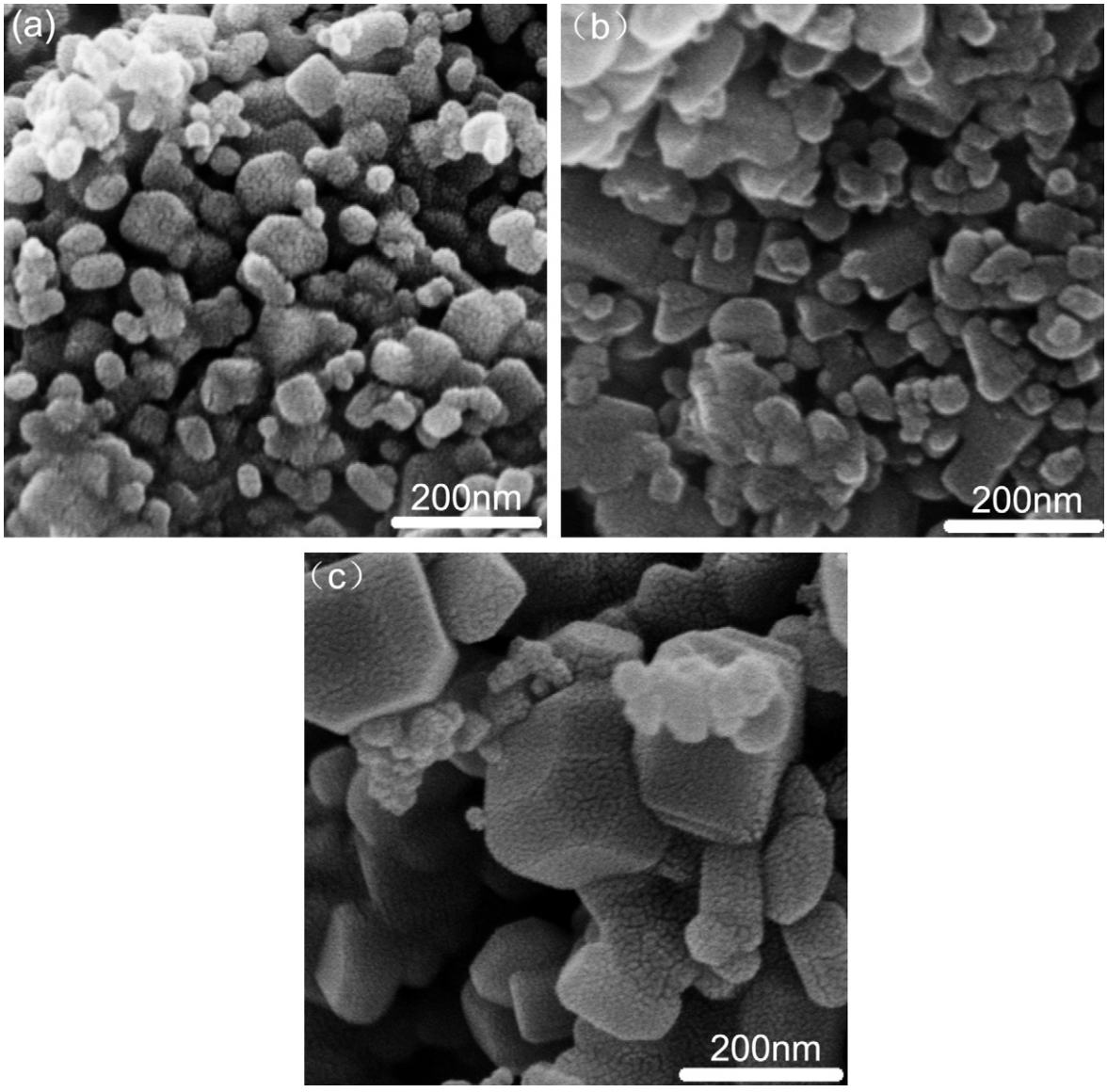

Fig. 6. FESEM images of products kept at 1200 °C for different heat preservation time, purified by hydrochloric acid and water. (a) 1 h (b) 2 h (c) 3 h.

increasing the proportion of $NaBH_4$ to some extent was necessary.

3.3. Effect of heat preservation time on final products

$LaCl_3$ and $NaBH_4$ were mixed with a molar ratio of 1:6 and were then kept at 1200 °C in vacuum for 1 h, 2 h and 3 h, respectively. XRD patterns of the products before purification were shown in Fig. 5. FESEM photographs of the products purified by hydrochloric acid and water were shown in Fig. 6.

From Fig. 5 we could see that impurity of $LaBO_3$ with a small quantity existed in the products and could not be eliminated simply by changing heat preservation time.

FESEM images in Fig. 6 showed us the growing process of LaB_6 grains. Increasing time from 1 h to 2 h, grains grew bigger and changed their shape from irregular to cubic. With heat preservation time longer than 2 h, there was an obvious tendency of grain coarsening.

Then we came to the conclusion that heat preservation time had a significant effect on grain size and the final shape. Longer time helped to form cubic grains with a regular shape and resulted in grain coarsening as well.

3.4. Optimized technology based on discussion above

Considering these three factors comprehensively, we finally adopted the 1:12 ratio of $LaCl_3$ to $NaBH_4$, reaction temperature 1200 °C and heat preservation time 2 h as the parameters of the optimized technology to prepare LaB_6 nanoparticles. In order to eliminate other impurities and agglomeration of LaB_6 grains, the products inside the graphic crucible underwent ultrasonic cleaning and were then purified by hydrochloric acid pickling and distilled water before observation. The XRD pattern of the as-prepared products after purification was presented in Fig. 7.

Every diffraction peak in Fig. 7 precisely occupied the position of standard θ value of LaB_6 cubic crystal system (space: pm3m (2 2 1)). According to Brag formula: $2d\mathrm{Sin}\,\theta = \lambda(\lambda = 1.5405\ \text{Å})$, eight different values of d were calculated out with eight given values of θ separately. They were in good correspondence with theoretical d values of standard LaB_6 crystalline lattices (JCPDS Card No: 34-0427). All the eight diffraction peaks could be obviously indexed as cubic crystal system of LaB_6. No impurities were observed. The strongest peak (1 1 0) was scanned slowly at the speed of $0.5^\circ\ \text{min}^{-1}$. The result was shown in the inserted image, according to which the average particle size was calculated to be about 66.7 nm (Scherer equation was used here since the grains were mostly cubic, as shown in Fig. 8.). Besides LaB_6, other products outside the graphic crucible which were not determined by XRD, such as NaCl, Na_2O_2 and B powder were found to deposit on the inside wall of furnace cover after reaction. The gas expelled out was proved to be hydrogen.

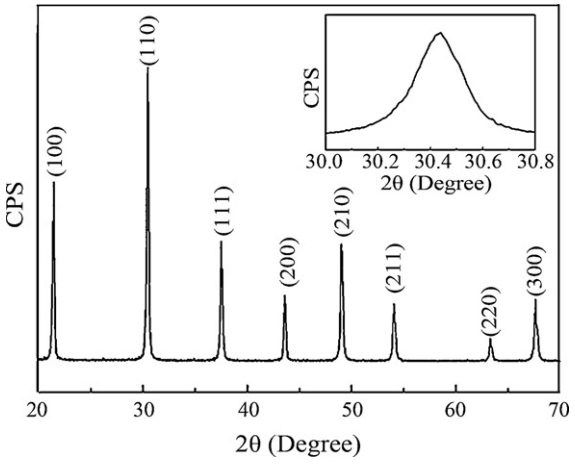

Fig. 7. XRD images of products gained via the optimized technology, purified by hydrochloric acid and water.

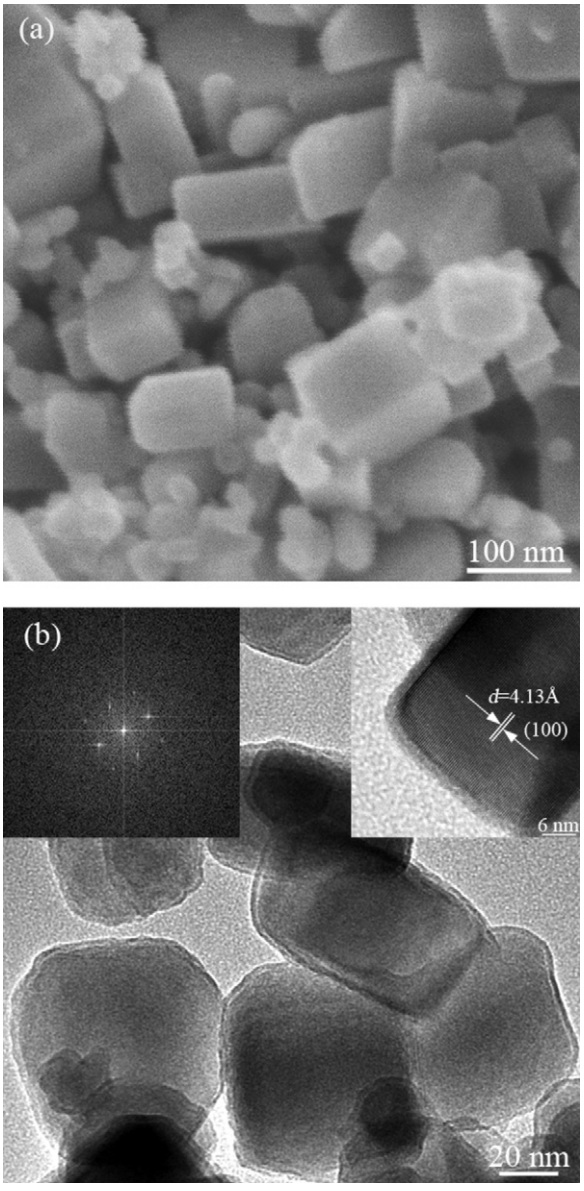

Fig. 8. Morphology and structure images of final products, purified by hydrochloric acid and water. (a) FESEM image of the products. (b) Low-magnification HRTEM image of pure LaB_6 nanoparticles. The left inserted image: Fourier conversion; the right one: lattice structure image from HRTEM.

Therefore the reaction equation could be described as follows:

$$6NaBH_4 \xrightarrow{400\,^{\circ}C\ \text{in vacuum}} 6Na + 6B + 12H_2 \quad (1)$$

$$LaCl_3 + 6NaBH_4 \xrightarrow{1200\,^{\circ}C\ \text{in vacuum}} LaB_6 + 3NaCl + 12H_2 + 3Na \quad (2)$$

The morphology and structure of the products were further studied by FESEM and HRTEM, as respectively, shown in Fig. 8a and b.

It could be seen from Fig. 8a that the products were mostly composed of cubic particles with sizes ranging from 20 nm to 100 nm. According to this figure, the mean grain size was estimated to be 69.8 nm. Fig. 8b was a low-magnification HRTEM image of the products, showing that the grains were nanosized and covered by amorphous oxide shells, which were estimated to be about 1.5–3 nm in thickness. Similar discovery was reported by Zhang [9] during the preparation of LaB_6 nanomaterials. Fourier conversion result of the grains was given by the left inserted image, proving the grains to be LaB_6 nanocrystals with (1 0 0) planes. The right inserted image depicted the crystalline structure. It clearly showed an interplanar distance of 4.13 Å, corresponding to the theoretical value 4.15 Å of LaB_6 (1 0 0) planes.

4. Conclusions

Reaction temperature had a great effect on final products. With temperature increased from 900 °C to 1200 °C, more LaB_6 grains with higher degree of crystallinity appeared, presenting less agglomeration and less impurities. Increasing the portion of reactant $NaBH_4$ could reduce the amount of impurity $LaBO_3$ and help LaB_6 grains form a regular shape. Longer heat preservation time helped to form cubic grains with a regular shape and resulted in grain coarsening size as well.

Based on the work above, we adopted the optimized technology for preparation of nanocrystalline LaB_6 in vacuum, consisting of a 1:12 molar ratio of $LaCl_3$ to $NaBH_4$, reaction temperature around 1200 °C and heat preservation time about 2 h. LaB_6 nanocrystals with a cubic shape and dominated (1 0 0) planes were then successfully prepared.

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