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Synthesis of single-crystalline lanthanum hexaboride nanocubes by a low temperature molten salt method

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HIGHLIGHTS

- A molten salt method was designed to prepare LaB_6 nanocubes.
- Single-crystalline LaB_6 nanocubes of 94.7 nm were successfully synthesized at 800 °C.
- The molten salt medium played a significant role in promoting formation and growth of LaB_6 nanocubes.

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ABSTRACT

A low temperature molten salt method was developed to prepare lanthanum hexaboride (LaB_6) nanocubes. Lanthanum trichloride ($LaCl_3$) and sodium borohydride ($NaBH_4$) were chosen as lanthanum and boron source respectively. A eutectic LiCl/KCl mixture was used as the molten salt medium. Single-crystalline LaB_6 nanocubes with a mean size of 94.7 nm were successfully synthesized by the molten salt method at 800 °C. X-ray diffractometer (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and Raman spectrophotometer (Raman) were used to characterize the composition, morphology and microstructure of the samples. To make clear of the role of molten salt medium in synthesis of LaB_6 nanocubes, a direct solid-state reaction of $LaCl_3$ and $NaBH_4$ was also conducted under the same reaction conditions.

1. Introduction

Lanthanum hexaboride (LaB_6), as a member of the rare-earth metal hexaborides (RB_6) family, is traditionally used as an excellent electron emitter in a large variety of devices, such as electron microscopy, free electron laser and vacuum electron beam welding machine [1–3]. Recently, LaB_6 nanoparticles have been found exhibiting a strong absorption of the near infrared (NIR) and high transmittance of visible light (VL) [4,5]. Therefore, LaB_6 nanoparticles are now considered to be applicable in reduction of solar heat gain fields, such as windows of vehicles and buildings which have a growing demand to filter out the infrared waves of the solar spectrum in modern life [6,7]. Moreover, the NIR absorption and VL transmittance of LaB_6 nanoparticles increase with decreasing particle size [8,9], and LaB_6 nanocubes exhibit a stronger NIR absorption than LaB_6 nanospheres [10].

However, it is challenging to prepare LaB_6 nanoparticles, let alone LaB_6 nanoparticles with definite shape like cube. In the past, many methods were used to prepare LaB_6 particles, such as a direct reaction of Lanthanum or its oxides with boron [11,12], a carbothermal reduction of lanthanum oxide and boron oxide or boron [13], a boron carbide reduction of lanthanum oxide [14] and a sodium borohydride reduction of Lanthanum oxide or lanthanum trichloride [15,16]. All these methods were conducted through a solid-state reaction which had a high reaction temperature above 1200 °C, and LaB_6 particles prepared by these methods generally had large size, low purity, and were easy to agglomerate together [11–16]. Besides, a molten salt electrolysis method was also used to prepare LaB_6 powders [17–19]. Lately, Zhang et al. reported that they had developed a novel and facile solid state reaction method to synthesize RB_6 (R = Ce, Pr, Nd) nanoparticles [20]. In this method, an appropriate amount of $RCl_3 \cdot 6H_2O$, B_2O_3 and excessive Mg were put into an autoclave, and then heat treated at the temperature as low as 400–500 °C for 12–48 h. Although RB_6 nanoparticles of 30 nm were eventually obtained by this method, high pressure and

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long time make it be unsuitable for commercial preparation of LaB_6 nanoparticles.

In this work, a novel and simple molten salt method (MS) was developed to synthesize LaB_6 nanocubes via the reaction of Lanthanum trichloride ($LaCl_3$) and sodium brohydride ($NaBH_4$) in a molten LiCl/KCl (45:55 wt) eutectic salt at 800 °C. Microstructures and compositions of LaB_6 nanocubes were investigated. Additionally, to make clear of the influences of molten salt medium on LaB_6 nanocubes, a direct solid-state reaction (DSR) of $LaCl_3$ and $NaBH_4$ without molten salt was also conducted under the same reaction conditions for comparison.

2. Materials and methods

In a typical process of MS, $LaCl_3 \cdot 7H_2O$ (99.0%, Alfa Aesar) was dried at 240 °C for 16 h, and then mixed with $NaBH_4$ (98%, Alfa Aesar) in an atomic ratio of La:B = 1:6. Later, the reactants along with LiCl/KCl (45:55 wt) eutectic salt (LiCl and KCl both have a high purity of 99.5%) were ground in an agate mortar. The mass ratio of reactants to salt was 1:10. The processed mixture was ultimately heated at 800 °C for 1 h under argon flow. The as-prepared product was washed and centrifugated several times with distilled water and finally dried at 80 °C for 12 h. A direct solid-state reaction of $LaCl_3$ and $NaBH_4$ without molten salt was conducted under the same reaction conditions.

The phase composition and crystal structure of the powders were identified by a Bruker Model D8. Advanced X-ray diffractometer (XRD) with Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å) operated at 40 mA and 40 kV. Raman spectra of the powders were measured on a LABRAM-HR Raman spectrophotometer using a 514 nm laser for excitation. The morphology and element composition of the powders were investigated using a scanning electron microscope (SEM, Quanta-200) operating at 10 kV equipped with an energy dispersive X-ray spectrometer (EDS). The microstructure and selected area electron diffraction (SAED) patterns of the powders were detected by a transmission electron microscope (TEM, JEOL-2010) using an accelerating voltage of 200 kV.

3. Results and discussion

The reaction between $LaCl_3$ and $NaBH_4$ can be expressed as reaction (1) [10,16]. Thermodynamic calculations were conducted in the standard state to estimate direction of this reaction. The changes in Gibbs' free energy and enthalpy of reaction (1) are shown in Fig. 1. The reaction is an endothermic process ($\Delta H > 0$) and spontaneous above ~ 410 °C (i.e., negative ΔG^0). Therefore, to ensure that $LaCl_3$ reacts with $NaBH_4$ in a molten salt liquid environment in this work, a eutectic LiCl/KCl (45:55 wt) mixture, which has a low melting point of 355 °C, was chosen as the molten salt medium to trigger reactions in the liquid state. Besides, the LiCl/KCl mixture is sustainable and water-soluble, so it will not be involved in the reaction of $LaCl_3$ and $NaBH_4$, and can be washed away by water.

$$LaCl_3 + 6NaBH_4 = LaB_6 + 3NaCl + 3Na + 12H_2 \quad (1)$$

Typical XRD patterns of LaB_6 powders synthesized by MS and DSR are presented in Fig. 2. Fig. 2a shows that all the diffraction peaks of MS-derived product can be easily indexed as a cubic crystal system of LaB_6 with space group *P*m-3m and lattice parameter of $a = 0.4160$ nm (calculated by the Bragg formula), and this result is in good agreement with the literature data (JCPDS 34-0427, $a = 0.4157$ nm). No other impurity peaks were observed, indicating that the product is pure phase LaB_6. However, there were some weak diffraction peaks of $LaBO_3$ (JCPDS 12-0762) besides LaB_6

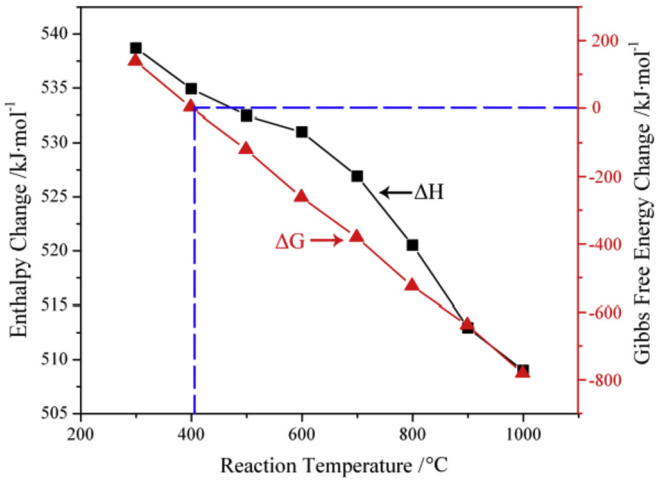

Fig. 1. Changes in Gibbs' free energy and enthalpy as a function of temperature for reaction (1). Data for the thermodynamics calculations come from Chase [21].

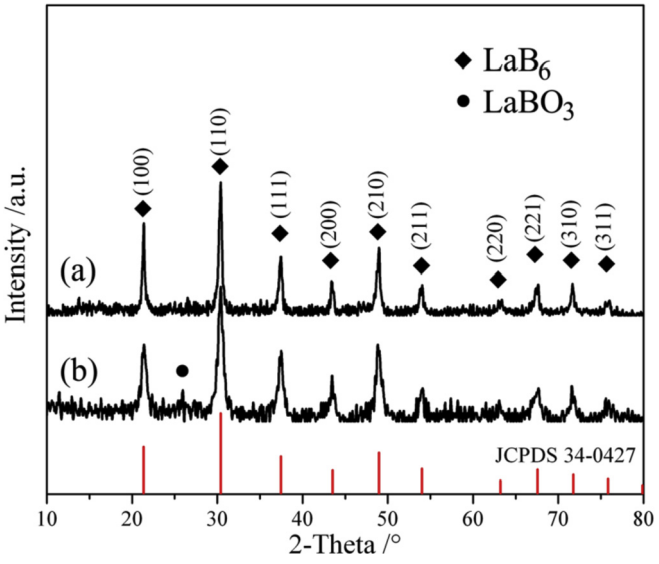

Fig. 2. XRD patterns of LaB_6 powders synthesized by (a) MS and (b) DSR.

in the DSR-derived product as shown in Fig. 2b. The formation of $LaBO_3$ may be ascribed to existence of trace oxygen in the reaction environment, which leads to oxidization of reactants or products. This result, to some extent, indicates that the molten salt medium of MS can protect the reactants and products from being oxidized during the chemical reaction. Additionally, the diffraction peaks of MS-derived LaB_6 were obviously sharper than that of DSR-derived LaB_6, indicating that crystal size of former was bigger than latter based on the Sherrer formula.

Morphology of LaB_6 powders was characterized by SEM as shown in Fig. 3. It is clear that LaB_6 powders fabricated by different routes have different morphologies. The MS-derived LaB_6 powders exhibited a good dispersion as depicted in Fig. 3a. Contrarily, the DSR-derived LaB_6 powders had an obvious agglomeration as depicted in Fig. 3b. Moreover, the MS-derived LaB_6 powders had a regular cubic shape with flat face, sharp corner and well-defined edge, and their size were basically identical. Their average size, measured by the Nano Measure software, was 94.7 nm. However, the DSR-derived LaB_6 powders had an irregular shape, and their size were obviously much smaller than that of MS-derived LaB_6