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Short Communication

Low temperature synthesis of LaB_6 nanoparticles by a molten salt route

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ABSTRACT

Lanthanum hexaboride (LaB_6) nanoparticles were successfully synthesized via the reaction of lanthanum trichloride ($LaCl_3$) and sodium borohydride ($NaBH_4$) in a molten KCl/LiCl eutectic salt. The changes in the phase composition and morphology of LaB_6 as a function of temperature were systemically investigated. By increasing the temperature from 600 °C to 800 °C, the crystallinity of LaB_6 particles increased and the sphere-like morphology of 49.0 nm changed to the cubic shape of 94.7 nm. Additionally, the microstructure and chemical composition of LaB_6 nanocubes were further characterized, and the possible synthesis mechanism of LaB_6 nanoparticles was proposed based on the experimental results.

1. Introduction

Lanthanum hexaboride (LaB_6) is known as an excellent electron emitter material due to its high melting point (2715 °C) [1], superior chemical and physical stability [2,3], constant electrical conductivity [4,5], and low work function (2.4–2.6 eV) [1,6]. Additionally, LaB_6 has a low evaporation rate and high carbon fouling resistance at high temperature. Hence, it can work a longer life span than that of traditional electron emitter material, such as tungsten [7]. All these wonderful properties make LaB_6 be widely used in many electrical devices including electron microscopy, free electron laser, vacuum electron beam welding machine and thermionic electron cathode [8–10]. Numerous studies are being conducted about LaB_6.

To date, many methods have been developed to synthesize LaB_6, such as a floating zone method to fabricate large LaB_6 single crystals [11,12], a hot pressing or spark plasma sintering to produce bulk LaB_6 polycrystalline [13,14], a chemical vapor deposition method to prepare LaB_6 nanowires [15,16] and a carbothermal reduction method to prepare micron size LaB_6 powders [17–19]. However, few methods are developed to synthesize LaB_6 nanoparticles, which have many superior properties, such as a strong absorption in the near infrared region [20], a great improvement in the density and strength of WC-10Co alloys by adding a small amount of LaB_6 nanoparticles [21]. More importantly, LaB_6 nanoparticles, with large specific surface area and high sintering activity, are believed to be the key to solving the problem of low sintering densification of bulk LaB_6 polycrystalline, which has puzzled researchers for years [13,22]. Therefore, it is worthwhile to develop a novel and efficient method to prepare LaB_6 nanoparticles.

In this paper, LaB_6 nanoparticles were successfully synthesized by a low temperature molten salt route. $LaCl_3$ and $NaBH_4$ were used as lanthanum and boron source, respectively. Eutectic LiCl/KCl (45:55 wt.) mixture, which has a low melting point of 355 °C, was chosen as a molten salt medium. Microstructures and compositions of LaB_6 nanoparticles were investigated.

2. Experimental procedure

The molten salt route used to synthesize LaB_6 nanoparticles consisted of four steps. First, $LaCl_3 \cdot 7H_2O$ powders (analytical reagent purity) were heat-treated at 240 °C for 16 h to remove crystalline water. Then, the anhydrous $LaCl_3$ and $NaBH_4$ (99.9% purity) were mixed thoroughly in a molar ratio of 1:6 and further combined in an agate mortar with LiCl/KCl (45:55 wt.), in a reactants/salt weight ratio of 1:10. The mixtures were subsequently heated to temperatures ranging from 600 °C to 1000 °C for 1 h under argon flow. After heating and subsequent cooling to room temperature, the reacted masses were washed repeatedly with distilled water to remove residual salts. The resultant product powders were dried overnight in a vacuum oven at 80 °C.

The phase composition and crystal structure of the powders were identified by a Bruker D8 X-ray diffractometer (XRD) with a step size of 4°/min. Morphologies of the powders were examined by a scanning electronic microscope (SEM, Quanta-200). Microstructures and chemical composition of the samples were detected by a transmission electron microscope (TEM, JEOL-2010) with an attached energy dispersive X-ray spectroscopy (EDS) system. X-ray photoelectron spectra (XPS) of the powders were recorded on a VG ESCALAB MKII X-ray photoelectron spectrometer, to further confirm surface chemical composition of the powders.

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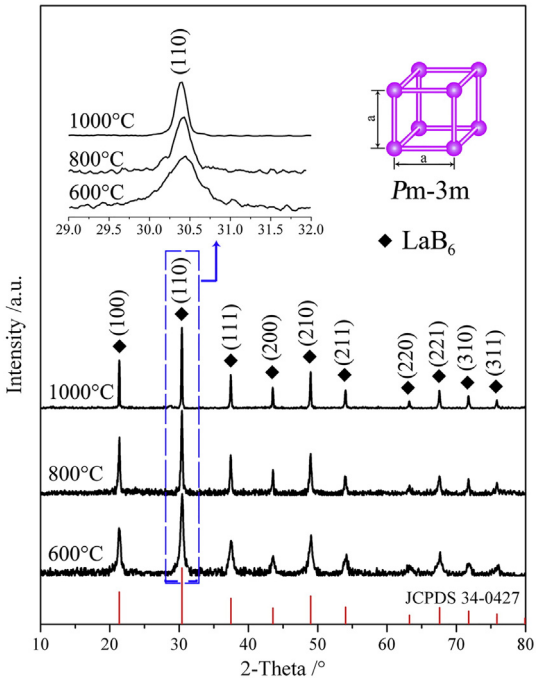

Fig. 1. XRD patterns of the LaB_6 powders fabricated by molten salt route at 600–1000 °C.

3. Results and discussion

XRD patterns of LaB_6 powders synthesized by molten salt route are shown in Fig. 1. All the diffraction peaks of the samples fabricated at different temperatures can be easily assigned to LaB_6 single phase with a simple cubic structure and a space group of *Pm-3m* (lattice parameter of $a = 4.160$ Å, calculated by the Bragg formula). This result is in good agreement with literature data (JCPDS 34-0427, $a = 4.157$ Å). No additional peaks from impurities were detected, indicating the high purity of the as-synthesized LaB_6. In this work, the possible reaction mechanism of $LaCl_3$ and $NaBH_4$ is shown as reaction (1) [23,24]. The product H_2 volatilized during the reaction, NaCl and Na were washed away by distilled water, leaving LaB_6 eventually. Additionally, sharper diffraction peaks were observed with increasing temperature, such as the (110) peaks as shown in Fig. 1. This phenomenon implied that the crystal size of LaB_6 powders grew with increasing temperature based on the Scherrer formula.

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

Fig. 2 shows the morphologies and particle size distribution of the LaB_6 powders fabricated by the molten salt route at different temperature. It is clear that the LaB_6 powders have a significant morphology change with increasing temperature. As shown in Fig. 2a, LaB_6 powders fabricated by the molten salt route at 600 °C had a sphere-like shape and uniform size. The mean size of the powders, measured by the Nano

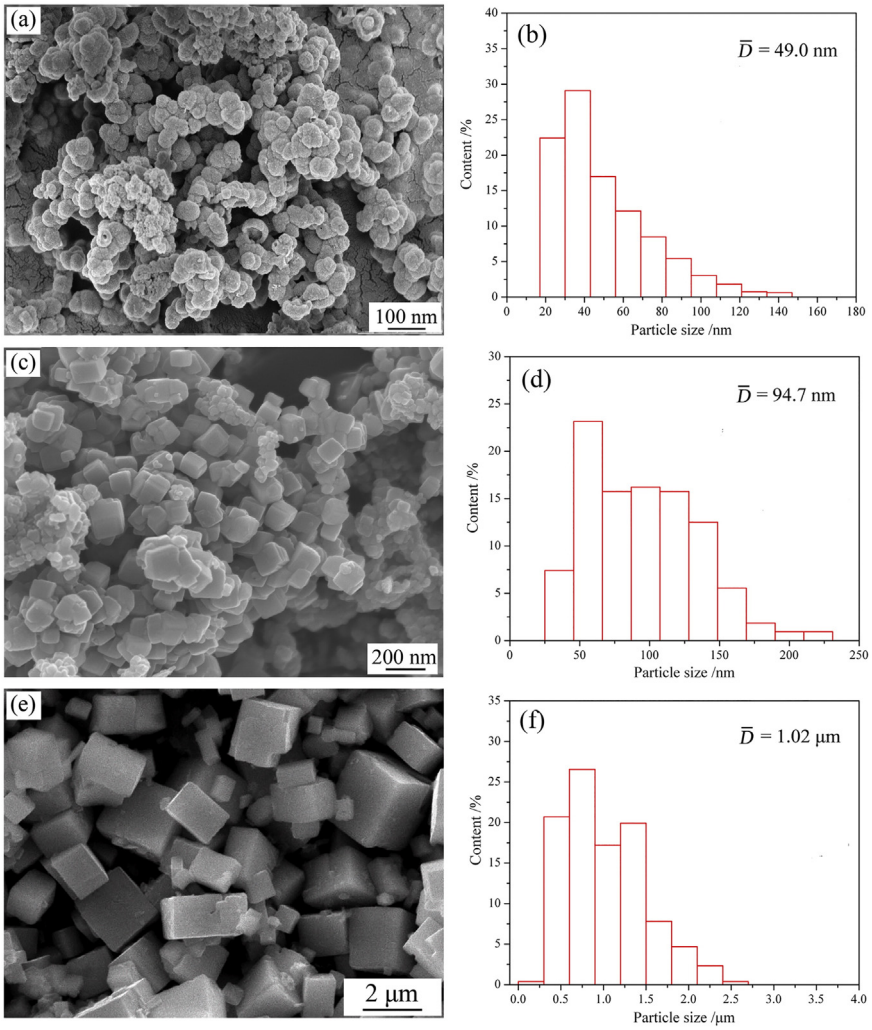

Fig. 2. Morphology and particle size distribution of LaB_6 powders fabricated by molten salt route at different temperatures: (a) and (b) at 600 °C, (c) and (d) at 800 °C, (e) and (f) 1000 °C.