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Quasi-spherical $LuBO_3$ nanoparticles: Synthesis, formation, and luminescence properties

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ABSTRACT

Quasi-spherical $LuBO_3$ nanoparticles have been successfully synthesized by a designed hydrothermal conversion method. The $Lu(OH)CO_3$ nanoparticles were first prepared by a simple homogeneous precipitation method. Subsequently, $LuBO_3$ nanoparticles were synthesized at the expense of the $Lu(OH)CO_3$ nanoparticles during a hydrothermal conversion process. The conversion process from the $Lu(OH)CO_3$ precursor to $LuBO_3$ nanoparticles was investigated by time-dependent experiments. Moreover, the as-obtained Eu^{3+} and Tb^{3+}-doped $LuBO_3$ products show strong characteristic red and green emissions under ultraviolet excitation and low-voltage electron beam excitation, respectively. This work sheds some light on the knowledge of conversion of different kind of lutetium compounds, and the luminescent properties have potential applications in fluorescent lamps and field emission displays. More importantly, this simple method is expected to allow the large-scale production of other complex rare-earth compounds with controllable morphologies and sizes, and exploration of the morphology and photoluminescence properties.

1. Introduction

In recent years, great efforts have been devoted to the synthesis of inorganic micro- and nanocrystals with controlled size and shape using various methods driven primarily by the fact that the shape and size of inorganic nano/microcrystals have tremendous effects on their properties [1]. Therefore, the preparation of nano/microsized inorganic materials with specific morphology, which may have a great influence on their physical properties, is required to meet different scientific and technological needs [2]. A variety of nano/micromaterials with different shapes and size have been prepared such as nanowires [3], nanorods [4], nanocubes [5], microurchin [6], nanopyramids [7], nanotriangles [8], microspindles [9], and nanodisks [10]. Thus, dramatic efforts have been dedicated to develop new methods for the fabrication of a range of high-quality inorganic functional nano/microstructures in different systems. In these fabrications, a promising chemical conversion route (sacrificial precursor method) has drawn our great attention [11]. To date, some well-defined nano/microcrystals, especially various hollow structures and one-dimensional nanomaterials, have been successfully prepared by this conversion route [12]. During the reaction, the precursors usually not only acted as the reactants but also controlled the shape of the products as a template.

Rare earth compounds have received extensive attention because of their potential applications in high-performance luminescent devices, magnets, catalysts, and other functionalmaterials, on the basis of optoelectronic and chemical properties originating from the 4f shell of rare earth ions [13]. In particular, rare earth orthoborates as luminescent materials have attracted much attention owing to their low toxicity, strong luminescence intensity, high chemical stability, and exceptional optical damage threshold [14]. For instance, rare earth orthoborates $LnBO_3$ (Ln = Y, and Gd) have proved to be very useful host lattices for the luminescence of Eu^{3+} and Tb^{3+}, which have found wide applications inmercury-free fluorescent lamps and various kinds of display devices [15]. Remarkably, lutetium (Lu) may be a more favorable cation than yttrium (Y) and gadolinium (Gd) for trivalent lanthanide dopant emission due to the intensity borrowing mechanism mixing the 4*f* and 5*d* orbitals of the Ln^{3+} ion via the lattice valence band levels [16]. Lutetium orthoborates ($LuBO_3$), due to its high density and high damage threshold, have been considered as a promising host matrix for RE ions substitution to produce phosphors, lasers or scintillators [17]. In fact, conventional solid-state reaction and sol–gel process-derived $LuBO_3{:}Eu^{3+}/Tb^{3+}$ phosphors have bad irregular shapes and agglomerated particles duo to the high annealing temperature and repeat grinding process, which will limit its dispersing stability and subsequent

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coating ability on the display panels [18]. Accordingly, $LuBO_3:Eu^{3+}/Tb^{3+}$ phosphors with homogeneous, monodispersed and well-defined morphology are highly desired.

Herein, quasi-spherical $LuBO_3$ nanoparticles have been successfully prepared for the first time through a hydrothermal conversion approach, without the use of any catalyst, organic solvent or surfactant. The structure, morphology, formation process, and luminescence properties of the as-obtained $LuBO_3$ samples were investigated in detail.

2. Experimental

2.1. Materials

The rare-earth oxides Ln_2O_3 (99.99%) (Ln = Lu, Eu) and Tb_4O_7 (99.99%) were purchased from the Science and Technology Parent Company of Changchun Institute of Applied Chemistry, and other chemicals were purchased from Beijing Fine Chemical Company. All chemicals were analytical-grade reagents and used as purchased without further purification.

2.2. Synthesis of $Lu(OH)CO_3$ nanoparticles precursor

The monodisperse colloid spheres of $Lu(OH)CO_3$ were prepared via a urea–based homogeneous precipitation process [19]. A total of 0.75 mL of $Lu(NO_3)_3$ (1 M) and 1.5 g of urea $CO(NH_2)_2$ were dissolved in deionized water. The total volume of the solution was about 50 mL. The above solution was first homogenized under magnetic stirring at room temperature for 1 h. The resultant solution was then reacted at 88 °C for 2 h in the oil bath. The obtained suspension was separated by centrifugation and collected after washing with deionized water several times and redispersed in 10 mL of deionized water.

2.3. Synthesis of $LuBO_3$ nanoparticles

0.26 g of H_3BO_3 (4 mmol) was first dissolved in 35 mL of deionized water, and then 10 mL of the as-prepared precursor suspension was added with continuous stirring. After additional agitation for 30 min, the mixture was transferred to a 50 mL autoclave and maintained at 180 °C for 24 h. The obtained white precipitate was washed with deionized water, centrifuged and dried at 60 °C in air.

The rare-earth doped $LuBO_3:Eu^{3+}/Tb^{3+}$ samples were prepared by the same procedures for the $LuBO_3$ sample except that a stoichiometric amount of $Eu(NO_3)_3$ or $Tb(NO_3)_3$ aqueous solutions was added to $Lu(NO_3)_3$ for the precursors in the initial stage as described above. Additionally, different hydrothermal treatment times (0.5 h, 5 h, and 12 h) were selected to investigate the conversion process from the precursor to the final products.

2.4. Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku-Dmax 2500 diffractometer with Cu Kα radiation (λ = 0.15405 nm). The morphologies and composition of the as-prepared samples were inspected on a field emission scanning electron microscope (FESEM, S4800, Hitachi) equipped with an energy-dispersive X-ray spectrum (EDX, JEOL JXA-840). Low- to high-resolution transmission electron microscopy (TEM) was performed using FEI Tecnai G^2 S-Twin with a field emission gun operating at 200 kV. Images were acquired digitally on a Gatan multiople CCD camera. The PL excitation and emission spectra were recorded with a Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The cathodoluminescent (CL) measurements were carried out in an ultrahigh-vacuum chamber ($<10^{-8}$ Torr), where the samples were excited by an electron beam at a voltage range of 1–5 kV with different filament currents, and the spectra were recorded on an F-7000 spectrophotometer. All measurements were performed at room temperature.

3. Results and discussion

3.1. Phase, structure and morphology

Fig. 1 shows the XRD patterns of the as-obtained $Lu(OH)CO_3$ and the hydrothermal products through the conversion process. It can be seen that the peaks of the precursor show two broad bands at 30° and 45° (Fig. 1A), which indicate that the as-formed precursor is amorphous. In order to understand the formation process of the $LuBO_3$ sample, the time-dependent experiments were performed. When the reaction was carried out at 180 °C for 0.5 h, the XRD pattern of the product shows the appearance of the diffraction peaks for the crystalline $LuBO_3$, and two broad bands at 30° and 45° also exist (Fig. 1B). By increasing the reaction time to 5 h, the crystallinity of the sample is increased (Fig. 1C). When the reaction time extends to 12 h or longer, the diffraction peaks of the samples become sharper and stronger with increasing reaction (Fig. 1C and D), that is, the crystallinity degree increases with increasing reaction time. When the reaction time was prolonged to 24 h, the XRD pattern of the product can be indexed easily as the hexagonal-vaterite phase of $LuBO_3$, in good agreement with the values in the standard cards JCPDS No. 74-1938 for $LuBO_3$.

Fig. 2 is SEM and TEM images observed from the as-formed precursor, clearly indicating that the as-formed $Lu(OH)CO_3$ precursor consists of nanoparticles. The diameter of the nanoparticles

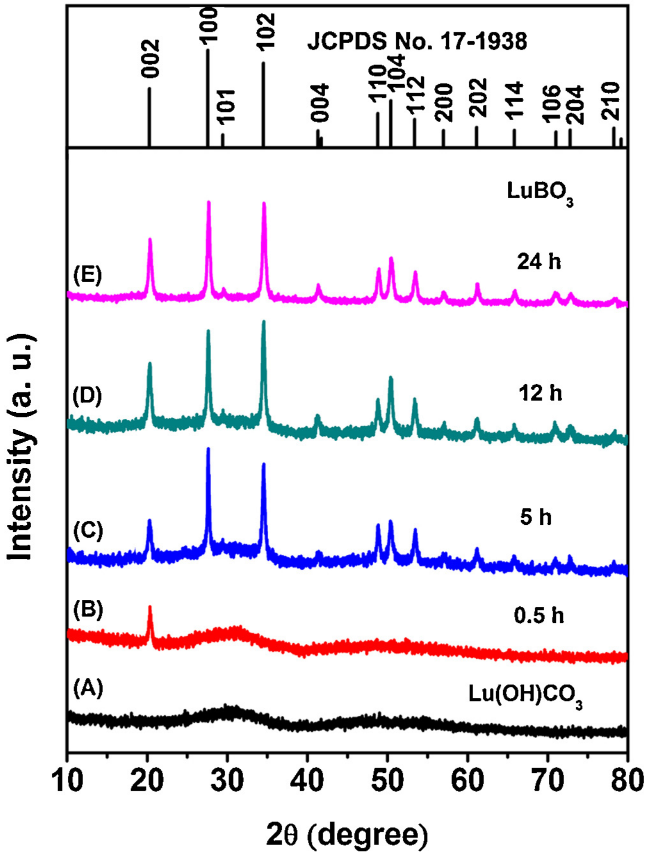

Fig. 1. XRD patterns of (A) $Lu(OH)CO_3$ precursor and the hydrothermal conversion products prepared at 180 °C for (B) 0.5 h, (C) 5 h, (D) 12 h, and (E) 24 h.