Applied Surface Science 330 (2015) 270–279

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Controlled synthesis of different multilayer architectures of $GdBO_3:Eu^{3+}$ phosphors and shape-dependent luminescence properties

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ARTICLE INFO

Article history:
Received 23 October 2014
Received in revised form
23 December 2014
Accepted 6 January 2015
Available online 13 January 2015

Keywords:
Hydrothermal method
Microcrystal
Crystal growth
Photoluminescence

ABSTRACT

Monodisperse pancake-like/flower-like/leaf-like $GdBO_3$ samples have been successfully synthesized via a designed hydrothermal conversion method using H_3BO_3, $Na_2B_4O_7{\cdot}10H_2O$, or $NaBO_2{\cdot}4H_2O$ as boron sources, respectively. It was found that different boron sources have crucial influences on the formation and morphology of the products. The $Gd(OH)_3$ nanorods precursors were prepared through a simple hydrothermal process, which then served as sacrificial templates for the fabrication of $GdBO_3$ micropancakes/microflowers/microleaves via a hydrothermal conversion process. FT-IR spectra confirm that vaterite-type $GdBO_3$ can be synthesized by this method. The possible formation mechanisms for different microstructures were put forward on the basis of a series of time-dependent control experiments. The products have similar stacked arrangements driven by the minimization of the interfacial and surface energy of the hydrothermal system. An investigation on the photoluminescence (PL) properties of $GdBO_3:Eu^{3+}$ samples with different morphologies indicates that the PL properties of as-obtained $GdBO_3:Eu^{3+}$ phosphors are strongly dependent on their morphology and crystallinity. The flower-like structure exhibits the strongest red emission.

1. Introduction

Synthesis of inorganic nano-/micro-materials with well-defined and controllable morphologies has been an important goal of modern materials chemistry, because the properties of nano-/micro-crystals depend not only on their composition, but also on their structure, phase, dimensionality, shape, and size distribution [1–3]. And so, controlling the morphologies and finding novel properties of materials have became important research issues in recent years. Up to now, great interests and tremendous efforts have been progressively devoted to the design and synthesis of inorganic nano-/micro-materials with unique and novel structures, allowing us not only to observe the unique properties of the materials but also to tune their chemical and physical properties as desired. Among a variety of morphologies, one-dimensional (1D) nano-/micro-materials, including wires, rods, belts, and tubes, have been extensively investigated due to their potential applications in a wide range of fields [4]. Two-dimensional (2D) nano-/micro-materials, including plates, disks, sheets and prisms, have potential applications in fields such as information storage, catalysis, sensors and luminescent devices [5]. And three-dimensional (3D) nano-/micro-materials have been explored for a new generation of advanced devices such as supercapacitors, fuel cells, and sensors [6]. Many methods have been used for the preparation of nano-/micro-structures, including hydrothermal synthesis [7], solid-state reaction [8], template-directed synthesis [9], sol–gel method [10], catalytic growth [11], electrospinning process [12], sonochemistry-assisted microwave synthesis [13], co-precipitation [14], etc. Among all synthetic methods, the hydrothermal synthetic method has showed an extraordinary ability in the controllable fabrication of inorganic nano-/micro-structures.

Nowadays, borate materials have attracted more and more attention due to their special optical properties, high stability, low synthesis temperature, and high ultraviolet and optical damage threshold [15]. Among a variety of borate phosphors, $GdBO_3:Eu^{3+}$ is one of the excellent and efficient phosphors available for the red primary of the color picture in plasma display panels and possibly be used in Hg-free lamp [16]. However, most of the previous works about the synthesis of lanthanide orthoborates are mainly concentrated on using H_3BO_3 as boron source to obtain different structures via hydrothermal process [17–20], and only limited information is

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http://dx.doi.org/10.1016/j.apsusc.2015.01.046
0169-4332/

available on using borate (such as $Na_2B_4O_7{\cdot}10H_2O$ or $NaBO_2{\cdot}4H_2O$) as boron source [21–24]. To the best of our knowledge, up till now, there are no systematic studies on using different boron sources to control different morphologies of $GdBO_3$ via a facile and general hydrothermal conversion method without using any surfactant or catalyst.

In this paper, for the first time, $Gd(OH)_3$ nanorods were used as precursors treated with different boron sources (H_3BO_3, $Na_2B_4O_7{\cdot}10H_2O$, or $NaBO_2{\cdot}4H_2O$) in the hydrothermal process to control different morphologies of $GdBO_3$. Furthermore, the structures, formation mechanisms and PL properties of the as-synthesized products have also been investigated in detail.

2. Experimental

2.1. Materials

$Ln(NO_3)_3$ (Ln = Gd, and Eu) aqueous solutions were obtained by dissolving the corresponding metal oxide in dilute HNO_3 solution under heating, respectively. All the other reagents are of analytical grade and used directly without further purification. Distilled water was used throughout.

2.2. Hydrothermal synthesis of $Gd(OH)_3$ nanorods

The $Gd(OH)_3$ nanorods precursors were prepared via a typical hydrothermal synthetic process. 10 ml $Gd(NO_3)_3$ (0.1 M) aqueous solution was added to 25 ml distilled water. Then 1 M NaOH aqueous solution was introduced into the solution until pH = 11.5. After further stirring, the resultant mixture was subsequently transferred into a 50 ml Teflon-lined autoclave. The hydrothermal reaction was conducted at 130 °C for 6 h. After the autoclave was cooled to room temperature, the obtained white products were washed with distilled water several times.

2.3. Synthesis of $GdBO_3$ micropancakes/microflowers/microleaves

In a typical procedure for the preparation of $GdBO_3$ micropancakes, the as-obtained 1 mmol of $Gd(OH)_3$ nanorods were firstly redispersed into distilled water by ultrasonic treatment. 10 ml H_3BO_3 (0.4 M) aqueous solution was dripped into the dispersion followed by further stirring. After that, the resultant mixture was subsequently diluted to 40 ml with distilled water and transferred into a 50 ml Teflon-lined autoclave. The hydrothermal reaction was conducted at 180 °C for 24 h. After the autoclave was cooled to room temperature, the obtained white products was washed with distilled water and ethanol and then dried in vacuum at 60 °C. The as-prepared product was denoted as **S1**. $GdBO_3$ microflowers were prepared in a manner similar to that for **S1**, except that $Na_2B_4O_7{\cdot}10H_2O$ instead of H_3BO_3 was used as the initiating material and reaction time was prolonged to 72 h, and the as-prepared product was denoted as **S2**. $GdBO_3$ microleaves were prepared in a manner similar to that for **S2**, except that $NaBO_2{\cdot}4H_2O$ instead of $Na_2B_4O_7{\cdot}10H_2O$ was used as the initiating material and the initial pH of the mixture was adjusted to pH = 10 using dilute nitric acid solution, and the as-prepared product was denoted as **S3**. The detailed experimental conditions and the corresponding morphologies and sizes of the $GdBO_3$ micropancakes/microflowers/microleaves are summarized in Table 1.

A similar process was employed to prepare Eu^{3+}-doped gadolinium compounds, except for adding a stoichiometric amount of $Eu(NO_3)_3$ instead of $Gd(NO_3)_3$ aqueous solution at the initial stage.

2.4. Characterization

All the samples were investigated by X-ray diffraction (XRD) measurements performed on a Rigaku D/max-II B X-ray diffractometer with monochromatic Cu K_α radiation. The morphology and composition of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi), employing the accelerating voltage of 10 kV. The infrared spectra of the samples was taken in KBr pressed pellets on a NEXUS 670 infrared Fourier transform spectrometer (Nicolet Thermo, Waltham, MA). The photoluminescence excitation and emission spectra were recorded with a Hitachi F-7000 spectrophotometer equipped with a 150 W Xe lamp as the excitation source. The quantum efficiency (QE) was measured using the integrating sphere on the time resolved and steady state fluorescence spectrometers

Table 1
Summary of the experimental conditions and corresponding morphologies and sizes of the $GdBO_3$ microplates/microflowers/microleaves.

Sample	Boron source	Gd/B molar ratio	T (°C)	pH	Time (h)	Morphology	Diameter (μm)/thickness (nm)
S1	H_3BO_3	1:4	180	–	24	Micropancakes	3.2/600
S2	$Na_2B_4O_7{\cdot}10H_2O$	1:8	180	–	72	Microflowers	2/500
S3	$NaBO_2{\cdot}4H_2O$	1:8	180	10	72	Microleaves	4–6/50

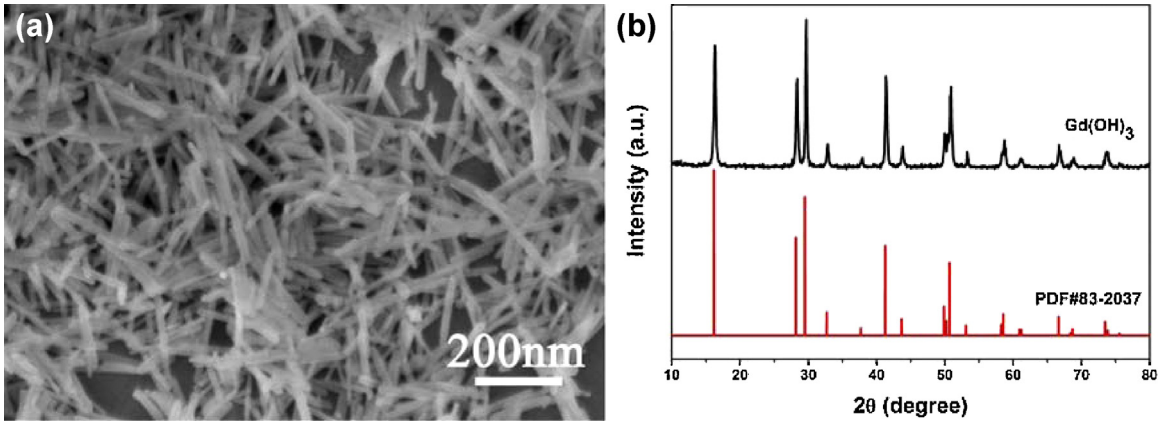

Fig. 1. SEM image (a) and XRD pattern (b) of as-obtained $Gd(OH)_3$ nanorods.