



Full length article

One-step solvothermal synthesis, a worm-shaped morphology and luminescence properties of green-emitting $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ nanophosphors



Fan Liu, Jingbao Lian*, Nianchu Wu, Jiao He, Xue Zhang, Feng Liu

School of Mechanical Engineering, Liaoning Shihua University, Fushun 113001, PR China

ARTICLE INFO

Article history:

Received 19 April 2017

Received in revised form 22 August 2017

Accepted 28 August 2017

Available online 12 September 2017

Keywords:

Yttrium oxysulfide

One-step solvothermal synthesis

Formation mechanism

Luminescence properties

ABSTRACT

The worm-shaped $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ nanophosphors have been successfully prepared via one-step solvothermal synthesis, using ethanediamine as the main solvent and sublimed sulfur powder as the source of sulfur without adding additional structure-directing reagents. XRD, FT-IR, FESEM, PL and CIE chromaticity diagram were used to characterize the obtained products. XRD results demonstrate that all diffraction peaks of the sample can be well indexed to pure hexagonal phase of $\text{Y}_2\text{O}_2\text{S}$ with optimal condition, i.e. the molar ratio of S/Y^{3+} $m = 10$, solvothermal temperature $T = 220^\circ\text{C}$ and synthetic time $t = 24$ h. When t varies from 2 h to 24 h, the morphology of $\text{Y}_2\text{O}_2\text{S}$ transforms from cauliflower-like structure to worm-shaped nanoparticles with the length of ~ 80 nm. The formation mechanism depending on t has also been proposed. Upon 250 nm ultraviolet (UV) light excitation, the worm-shaped $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ nanophosphors exhibit green emissions, corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($J = 6, 5, 4, 3$) transitions of Tb^{3+} ions. The quenching concentration is 7% and its corresponding lifetime is 1216 μs . The CIE chromaticity coordinates show the tuneable emission shifting from yellow green to yellowish green with increasing concentration of Tb^{3+} ions from 1% to 7%. Those results suggest that the worm-shaped $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ nanophosphors may have potential applications in X-ray intensifying screens, fluorescence and biomedical fields.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The rare earth (RE) compounds, existing in some stable forms including fluorides, oxides, sulphides, oxysulfides and oxysulfates, etc. have stimulated greatly interest due to their unique physical and chemical properties, such as a diode-pumped Yb,Y:CaF₂ laser [1], the special electronic level structures of REPO₄, REBO₃, REAlO₃ and RE₂O₃ (RE = La, Gd, Y, Lu, Sc) [2], the upconversion luminescence of Gd₂O₂S:Er,Tb [3] and a red phosphor of (La_{0.95}Eu_{0.05})₂O₂-SO₄ [4]. These special properties have made them critically important for various applications in medical imaging, cancer therapy, inorganic pigments, light-emitting diodes (LED) and X-ray detection devices [5–12].

Recently, Tb^{3+} ions doped RE₂O₂S (RE = Y, La and Gd) phosphors, known as efficient scintillation materials, have aroused great interest due to their hard radiation stability, high X-ray absorption and high conversion efficiency, which have been widely applied in X-ray intensifying screen and flat-panel X-ray imaging in medical diagnosis [13–15]. Conventionally, RE₂O₂S:Ln³⁺ (RE = La, Sm, Y, Gd; Ln = Eu, Yb, Er, Tb) luminescent materials (e.g. nanobelts,

nanofibers) were usually prepared by electrospinning synthesis [16], double-crucible method [17], thermal decomposition process [18], complicated-precipitation synthesis [19] or calcination the mixtures of their corresponding carbonate-hydroxide [20], oxide [21] or carbonate precursors [22] followed by a complicated sulfuration reaction at high temperature. Just as mentioned above, the pyrolysis of organometallic precursors is a common way to synthesize the target product. However, these methods were limited due to their complicated procedures. Moreover, it was also found that the luminescence efficiency, color purity and emission lifetime of RE-based compounds greatly depend on their crystallinity, morphologies, dimensions and sizes [23–26]. Therefore, it is of great significance to systematically investigate an effective synthetic method to design RE oxysulfide-based nano/micro particles with well defined shapes and excellent purities. According to previous literatures, hydro/solvothermal method is a widely used approach to control the morphology, dimension and size of nanostructures [27–29]. For example, Yu et al. have prepared uniform Gd₂O₂S flower-like nano-assemblies [30] through a novel one-pot mild (200–250 °C) solvothermal method with polyvinyl pyrrolidone (PVP) as the capping agent. To the best of our knowledge, studies for a controllable morphology of the worm-shaped $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$

* Corresponding author.

E-mail address: lianjingbao@aliyun.com (J. Lian).

nonaphosphors on the luminescence and crystal growing-up mechanism have little been reported.

In this paper, we firstly synthesized the worm-shaped $Y_2O_2S:Tb^{3+}$ nanophosphors by a simple, facial and effective one-step solvothermal method without adding additional structure-directing reagents. Ethanediamine was used as the main solvent and sublimed sulfur powder was used as the source of sulfur. The synthetic time T , the heating temperature T and the molar ratio of S/Y^{3+} m were discussed in detail for obtaining the target product and controlling its corresponding morphology. The growth mechanism and luminescence properties of $Y_2O_2S:xTb^{3+}$ ($x = 1\%$, 4% , 7% and 10%) were also investigated. It is expected that the worm-shaped $Y_2O_2S:Tb^{3+}$ nanophosphors will enrich their family and further expand their promising applicable fields.

2. Methods and characterization

$Yb(NO_3)_3 \cdot 6H_2O$ (99.99% purity), $Tb(NO_3)_3 \cdot 6H_2O$ (99.99% purity), ethanediamine, sublimed sulfur powder and absolute ethanol were used as the starting materials without further purification. Ethanediamine was purchased from Tianjin Zhiyuan Chemical Reagent Co. Ltd., China. The other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Firstly, a $Y(NO_3)_3$ ethanol solution with Y^{3+} ions concentration of 0.2 M was prepared by dissolving corresponding $Y(NO_3)_3 \cdot 6H_2O$ in absolute ethanol. Accompanied with vigorous stirring, then 5 mL $Y(NO_3)_3$ ethanol solution (0.2 M) was added dropwise into 65 mL ethanediamine solution containing a certain amount of sublimed sulfur to form a suspension solution with the molar ratio of 10:1 for $S:Y^{3+}$ (i.e. $m = 10$). After stirred for another 5 min, the as-obtained suspension solution was transferred to a 100 mL para poly phenol (PPL) lined stainless steel autoclave and then heated in an electric blast drying oven for solvothermal synthesis at $220^\circ C$ for 24 h ($T = 220^\circ C$ and $t = 24$ h). After naturally cooled to room-temperature, the product was washed and centrifugated with absolute ethanol for several times and then dried in air at $80^\circ C$ overnight successively. A diverse range of samples conducting at different synthetic time t , heating temperature T , initial S/Y^{3+} molar ratio m and a series of Tb^{3+} doped Y_2O_2S nanophosphors were also prepared in the same method.

The structure and phase analyses were identified on X-ray powder diffraction (XRD, D/max-RB) and Fourier transform infrared spectra (FT-IR) tools. XRD pattern was operating at 40 kV and 100 mA with $Co\ K\alpha = 1.789 \text{ \AA}$. FT-IR spectra were recorded in the region of $4000\text{--}400\text{ cm}^{-1}$ using a FT-IR-660+610 spectrophotometer by the KBr method. Morphology and particle size were observed by field-emission scanning electron microscopy (FESEM) using Hitachi SU8000 microscope operated at an acceleration voltage of 20 kV. Photoluminescence (PL) spectra and decay time were measured using a Hitachi F-7000 fluorescence spectrophotometer equipped with IBH TemPro fluorescence lifetime measurement system. The CIE coordinates were calculated from the spectra based on the 1931 CIE standard for colorimetry.

3. Results and discussion

3.1. Phase formation mechanism and optimization for synthetic parameters

As discussed in previous work [31], hard-soft acid-base theory (HSAB) is a valid qualitative principle for understanding the syntheses of RE-based compounds. According to HSAB, the trivalent RE oxysulfide-based compounds have a poor affinity between hard acids and soft bases, specially with the only S^{2-} soft base as anion and RE^{3+} hard acid as cation. Therefore, the formation

of RE oxysulfide-based compounds remains a challenge. In order to obtain the target product (Y_2O_2S) through one-step solvothermal method, a series of relatively larger concentrations of sulfur were added to form a high sulfur potential energy, as shown in Fig. 1. Moreover, the solvothermal treatment temperature T and synthetic time t were also conducted in Figs. 2 and 3, respectively.

Fig. 1 shows the XRD patterns of as-synthesized samples in the presence of varying mole ratios m ($m = 1, 5$ and 10) with other parameters being constant, namely $T = 220^\circ C$ and $t = 24$ h. At a small value of m , the XRD pattern (Fig. 1(a)) represents amorphous with a low degree of crystallinity. With increasing the value of m to 5 (Fig. 1(b)), the broad peak (near at 29.16°) splits into two clear peaks centered at 27.18° and 29.17° , indicating a yttrium oxysulfide has basically formed. When the value of m further increases to 10 (Fig. 1(c)), the clear diffraction peaks can be well matched with the data according to standard JCPDS No. 00-24-1424 (Fig. 1(d)), suggesting the formation of hexagonal Y_2O_2S phase have been finished. Obviously, it shows the growth tendency toward Y_2O_2S phase from Fig. 1(a)–(c), indicating the well crystallization can be obtained with increasing the value of m . Therefore, the optimal S/Y^{3+} molar ratio was chosen as $m = 10$ in the present study.

Fig. 2 shows the XRD patterns and their corresponding FT-IR spectra of the samples prepared at temperatures of $120^\circ C$, $170^\circ C$ and $220^\circ C$ with $m = 10$ and $t = 24$ h. There are two broad peaks near $2\theta = 29.83^\circ$ and 48.72° in the curve of Fig. 2(a), indicating the sample was composed of amorphous yttrium compound. After solvothermal temperature is treated at $170^\circ C$, the sample

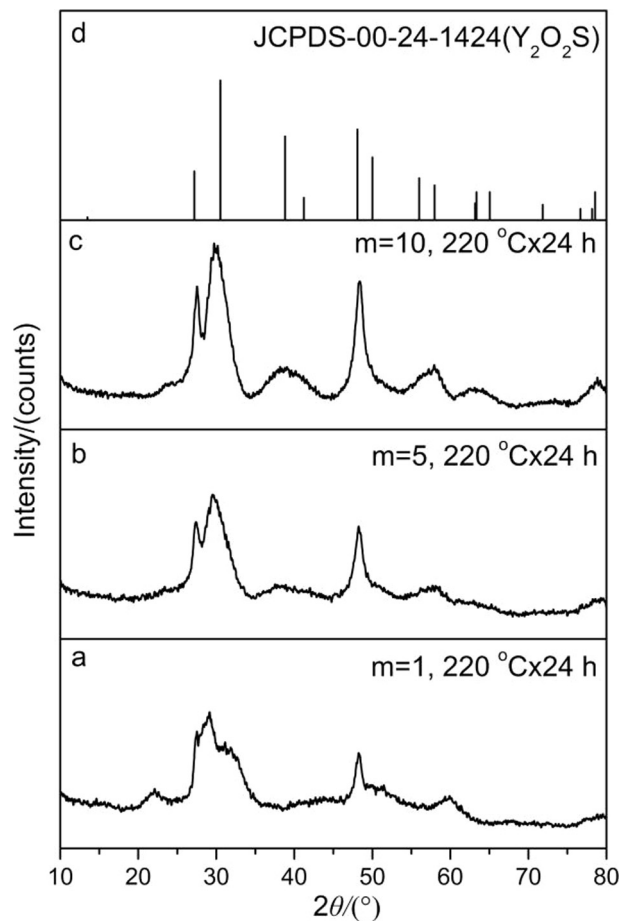


Fig. 1. XRD patterns of the Y_2O_2S samples obtained from different initial sulfur concentrations with $T = 220^\circ C$ and $t = 24$ h: (a) $m = 1$; (b) $m = 5$; (c) $m = 10$. The pattern of (d) is the data of Y_2O_2S with JCPDS card No. 00-24-1424 for comparison.

Download English Version:

<https://daneshyari.com/en/article/5007294>

Download Persian Version:

<https://daneshyari.com/article/5007294>

[Daneshyari.com](https://daneshyari.com)