Journal of Solid State Chemistry 196 (2012) 187–196

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

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

Solvothermal synthesis and tunable luminescence of Tb^{3+}, Eu^{3+} codoped YF_3 nano- and micro-crystals with uniform morphologies

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ARTICLE INFO

Article history:
Received 8 March 2012
Received in revised form
28 May 2012
Accepted 3 June 2012
Available online 9 June 2012

Keywords:
YF_3
Solvothermal synthesis
Morphology evolution
Energy transfer

ABSTRACT

Tb^{3+}, Eu^{3+} codoped YF_3 nano- and micro-crystals with the morphologies of ellipsoid-like nanoplate, spindle, sandwich-structural rhombus and nanoaggregate were synthesized through a solvothermal method. The morphologies of the prepared products can be tailored by controlling the volume ratio of ethylene glycol (EG) to H_2O, solvent type or the reaction time. A possible formation mechanism of the sandwich-structural rhombus like YF_3 phosphor was proposed. The emitting colors of YF_3:Tb^{3+},Eu^{3+} phosphors can be easily tuned from yellowish green, yellow to orange by increasing Eu^{3+} concentration. The energy transfer from Tb^{3+} to Eu^{3+} in YF_3 phosphors was studied. It was found that the interaction type between Tb^{3+} and Eu^{3+} is electric dipole–dipole interaction.

1. Introduction

Generally, the physical and chemical properties of inorganic luminescent materials are directly related not only with their chemical compositions, crystal phases but also the surface statuses, dimensions, sizes and morphologies of the phosphor grains [1,2]. Therefore, controllable synthesis has attracted considerable interest during the past decades [3–5]. By far, a variety of efforts have been devoted to developing numerous convenient and efficient approaches for the fabrications of multifarious inorganic luminescent materials with different shapes and sizes, such as nanowires, nanorods, nanotubes, nanocubes, nanoflowers, nanoplates, etc [6–11]. Among these synthesis techniques, the most popular ones for controllably preparing novel nano- and micro-structures involve ionic liquid, arc discharge, laser ablation, and biotemplate, as well as template-directed methods. Nevertheless, the above-mentioned synthesis routes call for some special instruments or harsh conditions, and that sometimes lead to impurities due to the incomplete removal of the templates. By contrast, hydrothermal or solvothermal synthesis routes are more promising than the conventional methods, since the products with various morphologies and regular shapes can be obtained by hydrothermal or solvothermal techniques, meanwhile their costs are usually rather low, thus hydrothermal and solvothermal routes have been widely adopted in recent studies on novel nano- and micro-structured inorganic luminescent materials [2,11].

The fluoride luminescent materials have attracted much attention due to their unique physical and chemical properties, for example low phonon energy, high ionicity, high resistivity, and high anionic conductivity [12–14]. The fluoride functional materials have wide potential applications in optics, phosphors, biological labels, and lenses, as well as components of insulators, gate dielectrics, wide-gap insulating overlayers, and buffer layers in semiconductor-on-insulator structures [15–17]. Yttrium trifluoride (YF_3) is one of the most important hosts, which has low refractive index (around 1.5) and wide band gap (>10 eV), and is optically transparent over a wide wavelength range from mid-infrared (20 μm) to vacuum ultraviolet (120 nm) [18,19]. YF_3 doped with trivalent lanthanide ions are also potential candidates as efficient phosphors due to their capability of producing efficient visible emission under vacuum UV irradiation [20,21]. Moreover, the ionic radius Y^{3+} is similar to other rare earth ions, thus high accommodation of rare earth luminescent centers can be expected without adding charge compensators [22,23].

In the present work, we tend to study on the synthesis and spectroscopic properties of Eu^{3+}/Tb^{3+} codoped nano- and micro-crystals YF_3. Tb^{3+}/Eu^{3+} codoped nano- and micro-crystals YF_3 with different morphologies, for instance ellipsoid-like nanoplate, spindle, sandwich-structured rhombus and nanoaggregate, were obtained through solvothermal process. The effects of various experimental conditions, such as the EG/H_2O volume ratio, type of

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http://dx.doi.org/10.1016/j.jssc.2012.06.004

solvent and reaction time, on the morphology of the products were discussed in detail. Both the emissions from Eu^{3+} and Tb^{3+} were observed in the sandwich-structural rhombus like $YF_3:Tb^{3+}/Eu^{3+}$ phosphors. The energy transfer behavior between Eu^{3+} and Tb^{3+} was studied. According to the Dexter's energy transfer theory the physical nature of energy transfer between Tb^{3+} and Eu^{3+} was confirmed to be electric dipole–dipole interaction. It was also found that the emission chromaticity of Tb^{3+}/Eu^{3+} codoped YF_3 phosphors can be tuned from yellowish green to yellow and followed to orange with increasing Eu^{3+} concentration.

2. Experimental

2.1. Reagents

All chemical reagents used in this work are analytical grade except for the spectrographically pure Eu_2O_3, Tb_4O_7 and Y_2O_3. The rare earth nitrates including $Eu(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 6H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were prepared through re-crystallization process. The detailed re-crystallization procedure was described as follows. First, the rare earth oxides including Eu_2O_3, Tb_4O_7 and Y_2O_3 were dissolved in 6 mol L^{-1} nitric acid, respectively. Then the corresponding solutions of rare earth nitrates were re-crystallized for three times. Finally, $Eu(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 6H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were obtained when the re-crystallized products were well dried in vacuum at 90 °C for 12 h.

2.2. Synthesis

Tb^{3+}/Eu^{3+} codoped YF_3 nano- and micro-crystals were synthesized by a solvothermal process. In a typical process, $Eu(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 6H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ (Eu: Tb: Y=0.05: 0.05: 0.90) were dissolved in 60 mL of EG under magnetic stirring to form a transparent solution I. Then, 6 mmol of NH_4HF_2 was added in 10 mL of distilled water to form solution II. After vigorous stirring for 30 min, solution II was dropped slowly in solution I, the white precipitation appeared at once. After additional agitation for 30 min, the as-obtained suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave, which was sealed and then maintained at 140 °C for 12 h. As the autoclave cooled to room temperature naturally, the white precipitate was separated by centrifugation and washed with distilled water and ethanol in sequence. Finally, the precipitate was dried in a vacuum condition at 80 °C for 12 h to obtain the Tb^{3+}/Eu^{3+} codoped YF_3 nano- and micro-crystals. Additionally, different solvothermal treatments by changing the volume ratio of EG to distilled water, the solvent and the reaction time at 140 °C were carried out to investigate the morphological dependence of the Tb^{3+}/Eu^{3+} codoped YF_3 phosphors on the reaction conditions.

2.3. Characterization

The crystal structure of the prepared samples was examined by using X-ray diffraction (XRD) carried out on an XRD-6000 (Shimadzu, Japan) powder diffractometer with Cu $K_{\alpha 1}$ radiation (λ=0.15406 nm) source. The XRD data in the 2θ range from 10° to 70° were collected by using a scanning mode with a scanning step of 0.02° and a scanning rate of 4.0 °min^{-1}. In the XRD measurements the single crystal silicon was used as an internal standard. The particle size and morphology were inspected by using a Japan Hitachi S-4800 field emission scanning electron microscopy (FE-SEM). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were recorded using a JEM-2100 with a field emission gun operating at 200 kV. Images were acquired digitally on a Gatan multiple CCD camera. Photoluminescence (PL) emission, excitation spectra and fluorescent decay curves were recorded with a Hitachi F-4600 spectrophotometer equipped with a 150 W xenon lamp as an excitation source. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Crystal structure and morphology of the prepared products

To check the composition and crystal structure of products, the XRD patterns were measured. It was found that all the samples display similar profile but different diffraction intensity. This fact implies that the doping concentration of rare earth ions and the synthesis conditions do not cause obvious change in the crystal structure and composition of products. For example, Fig. 1 shows the XRD patterns for 5 mol% Tb^{3+} single-doped (a) and 5 mol% Tb^{3+}/5 mol% Eu^{3+} codoped (b) YF_3 phosphors prepared through solvothermal process with EG/H_2O volume ratio of 6/1 at 140 °C for 12 h. In Fig. 1, all the diffraction peak positions can be readily indexed to a pure orthorhombic phase of YF_3 [space group: *Pnma* (62)] reported in JCPDS card No. 74-0911. In addition, no any peaks belonging to impure phases are observed, suggesting that the prepared products by solvothermal method are pure and single phase YF_3.

The FE-SEM was used to characterize the morphology and particles size of the prepared phosphors. It should be mentioned that introduction of the dopants (Tb^{3+} and Eu^{3+}) into the YF_3 host does not cause the change of the morphology of the YF_3 products. Herein, we only take YF_3 doped with 5 mol% Tb^{3+}/ 5 mol% Eu^{3+} as typical example to explore the morphology evaluation of the products. Fig. 2(a) and (b) depicts the low- and high-magnification FE-SEM images of YF_3 phosphor doped with 5 mol% Tb^{3+} and 5 mol% Eu^{3+} prepared at 140 °C for 12 h under the condition of EG/H_2O volume ratio of 6/1. As shown in Fig. 2(a), it can be found that monodisperse rhombus particles with sandwich structure can be prepared via the solvothermal route. The average two diagonal line lengths of rhombus particles are about 200 and 140 nm, respectively. The thickness of sandwich structure is around 70 nm. In addition, from the high-magnification FE-SEM image in Fig. 2(b), it can be clearly found that the surface of the rhombus particles is not smooth and contains many nanoparticles. In order to further inspect the morphology of the prepared YF_3:5 mol% Tb^{3+}/5 mol% Eu^{3+}, the TEM and HRTEM were carried out and typical images are shown

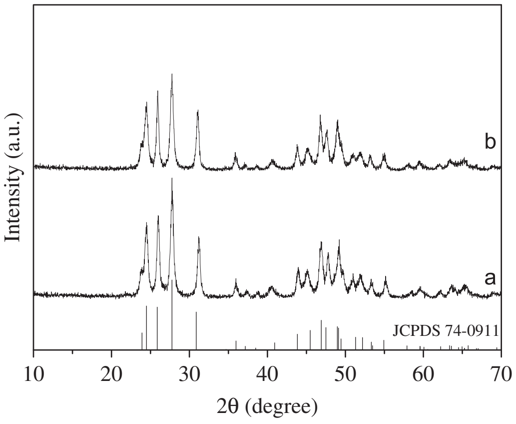

Fig. 1. XRD patterns of the prepared $YF_3:Tb^{3+}$ (a) and $YF_3:Tb^{3+}, Eu^{3+}$ phosphors (b).