



Sr₅(PO₄)₃Cl:Eu²⁺ with multiform morphologies and sizes: Hydrothermal synthesis and luminescent properties



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ABSTRACT

Sr₅(PO₄)₃Cl:Eu²⁺ nano/microcrystals with a variety of morphologies, such as nanorod, submicrospheres, nanoparticles, and nanospheres, have been synthesized via a facile hydrothermal route. The effect of phosphate source and surfactant on the morphologies and sizes has been studied. A systematic study on the photoluminescence of Sr₅(PO₄)₃Cl:Eu²⁺ with different microstructures has shown that the optical properties of these phosphors are strongly dependent on their morphologies and sizes. This synthetic methodology provides a new gateway to other Eu²⁺ doped luminescent materials.

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1. Introduction

Generally, the physical and chemical properties of nano/microsized inorganic materials depend not only on their chemical composition, but also on their structures, including phase, size, shape, and dimensionality [1–3]. So the shape-controllable synthesis of inorganic nano- or microcrystals has aroused considerable attention owing to their useful properties, which allow for applications in optics, electrics, magnetic, and optoelectronic devices [4–6]. An increasing number of nano- or micromaterials with different shapes and sizes have been prepared, such as wires [7], cubes [8], spheres [9], pyramids [10], triangles [11], and nanodisks [12]. Two general synthesis strategies have been employed for the shape controlled synthesis of nanomaterials: (i) the template method, which employs either hard templates such as anodic aluminum oxide (AAO) and polymeric core supports, or soft templates such as micelles and organic additives [13–16] and (ii) the template-free method [17,18]. Among these fabrications, the use of organic additives as the “shape modifier” is a common strategy to adjust and control the morphology and size of the products. Organic molecules are known to either promote or inhibit crystal growth through modifying crystal growth dynamically. By properly choosing organic additives that might have specific molecular complementarities with their inorganic counterparts, the growth of inorganic crystals can be rationally directed to yield products with desirable morphologies and/or hierarchical structures [19].

The M₅(PO₄)₃X (M = alkaline earths; X = F[−], Cl[−], Br[−] or OH[−]) type of apatite materials has been extensively studied for their technological importance, especially fluoroapatites and chloroapatites as phosphor materials and laser hosts and hydroxyapatites as biocompatible materials [20–22]. Among the various apatite materials, Sr₅(PO₄)Cl is a good host lattice for luminescence and laser materials. Sr₅(PO₄)Cl:Eu²⁺ is an important representative phosphor. It is a highly efficient luminescent material, used as the blue component in high-efficiency compact fluorescent lamps, white LEDs, and backlight for desktop monitors and LCD TVs because of its low price, environmental friendliness, good thermal stability, and high quantum efficiency [23]. Along with the progress of nano-science and nanotechnology, various synthesis techniques have been developed for the preparation of Sr₅(PO₄)Cl:Eu²⁺ so that it can be suitable for use in nanoscale electronic or optoelectronic devices.

In our previous work, Sr₅(PO₄)Cl:Eu²⁺ nanobundles have been reported [24]. Herein, we report the morphology-controlled synthesis of Sr₅(PO₄)Cl:Eu²⁺ blue phosphors through a facile and mild hydrothermal process. The effect of phosphate source and surfactant on the morphologies and the photoluminescence properties of Sr₅(PO₄)Cl:Eu²⁺ has been discussed.

2. Experimental

The rare earth oxide Eu₂O₃ (99.99%) was purchased from Shanghai Yuelong New Materials Co., Ltd., and other chemicals were purchased from Beijing Chemical Co. All chemicals are of analytical grade reagents and used directly without further purification. Rare earth nitrate stock solution of 0.05 M was prepared by dissolving the corresponding

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metal oxide in nitric acid at elevated temperature. In a typical procedure, 0.24 mmol SrCl_2 was first dissolved into 1 mL water by ultrasonic. 25 mL ethanol with 0.2 mmol $\text{Eu}(\text{NO}_3)_3$ was then added into the solution under stirring. Thereafter, 1.0 g (0.025 mmol) of poly(vinyl pyrrolidone) (PVP K30, $M = 40,000$) and 2 mL $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (>50%) were introduced into the above solution in sequence. Afterward, a solution of H_3PO_4 (0.1 mL, ≈ 1.5 mmol, 85%) in 10 mL anhydrous ethanol was added dropwise. After vigorous stirring for 30 min, the liner was put into the autoclave and the suspension was degassed with the $\text{N}_2\text{-H}_2$ ($V/V = 9/1$) for 30 min. The autoclave was finally maintained in an electric oven at 180 °C for 24 h. After cooled to room temperature naturally, the resulting white powder product was carefully collected by centrifuged (6000 g/min) and washed several times with deionic water and absolute ethanol. The final product was dried in air at 60 °C for 12 h. The as-prepared product was denoted as S2. Other samples were prepared by the similar procedure, except for different phosphate sources and organic additives. The experimental conditions are summarized in Table 1.

Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 focus X-ray powder diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15405$ nm). Fourier transform infrared spectroscopy (FT-IR) spectra were measured with Perkin-Elmer 580B infrared spectrophotometer with the KBr pellet technique. The size and morphology of the samples were inspected using a field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan). Photoluminescence (PL) excitation and emission spectra were recorded with a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source at room temperature.

3. Results and discussion

3.1. Phase identification

Fig. 1 shows the XRD patterns of the samples synthesized with H_3PO_4 and triphenyl phosphate (TPP) as the phosphate sources, respectively. All the diffraction peaks of the samples can be assigned to the standard data of $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ (space group $P63/m$). In addition, no peaks of impurities were detected, indicating that Eu^{2+} ions have been effectively incorporated into the $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ host lattice.

Fig. 2 shows the FT-IR spectra of the samples. All the samples have similar absorption peaks at 459, 559, 592, 949, 1027, 1072, 1631, and 3442 cm^{-1} , which can be ascribed to the ν_1 , ν_2 , ν_3 , and ν_4 bending or stretching vibration of P–O mode [25]. The bands centered at about 1631 and 3442 cm^{-1} can be assigned to the water adsorbed on the surface of the samples. There are two additional peaks at 2854 and 2924 cm^{-1} for the samples synthesized with oleyl amine as a surfactant, which are ascribed to the symmetric and antisymmetric methyl stretches [26]. This result indicates that there are surfactant residua in the samples synthesized with oleyl amine as a surfactant.

3.2. Morphology

Raw materials and surfactant can influence the morphologies and microstructures of the products. So the influence of the fluoride source and surfactant on the morphologies and luminescence properties was discussed in this paper.

Table 1

Parameters of the representative experiments and the morphologies and sizes of the corresponding products.

Sample	PO_4^{3-} source	Organic additives	Morphology	Diameter (nm)
S1	H_3PO_4	Oleyl amine	Nanorod	44–130
S2	H_3PO_4	PVP	Submicrospheres	144–360
S3	Triphenyl phosphate (TPP)	Oleyl amine	Nanospheres	25–36
S4	TPP	PVP	Nanoparticles	27–54

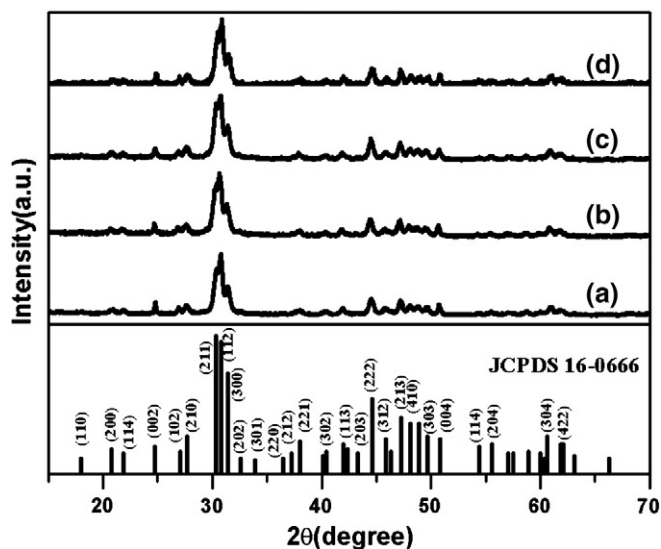


Fig. 1. XRD patterns of $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ samples with different PO_4^{3-} sources and surfactants. (a) H_3PO_4 as source and oleyl amine as surfactant; (b) H_3PO_4 as source and PVP as surfactant; (c) TPP as source and oleyl amine as surfactant; (d) TPP as source and PVP as surfactant.

3.2.1. H_3PO_4 as a phosphate source

Fig. 3A and B illustrates the representative SEM images of samples synthesized with H_3PO_4 as a phosphate source. When the oleyl amine was used as a surfactant, the obtained samples were composed of nanorods with the size between 44 and 130 nm in length and 25 and 39 nm in diameter (Fig. 3A). When the PVP was used as a surfactant, the morphology of the products varies greatly. It can be clearly seen from Fig. 3B that there is a large quantity of microspheres over the entire surface of the substrates. An analysis of a number of the microspheres shows that the diameter is between 144 and 360 nm. Further investigation shows that the microspheres are composed of nanoparticles with an average diameter of about 20 nm.

3.2.2. TPP as a phosphate source

Fig. 3C and D shows the SEM images for the samples synthesized with TPP as a phosphate source. When the oleyl amine was used as a surfactant, the obtained samples are nanospheres with a diameter

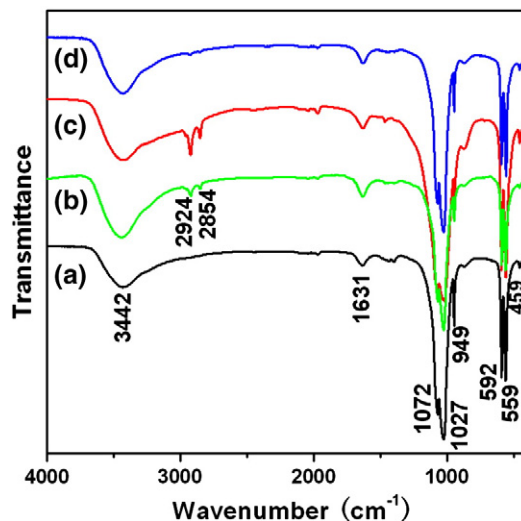


Fig. 2. FT-IR spectra of $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ samples with different PO_4^{3-} sources and surfactants. (a) H_3PO_4 as source and PVP as surfactant; (b) H_3PO_4 as source and oleyl amine as surfactant; (c) TPP as source and oleyl amine as surfactant; (d) TPP as source and PVP as surfactant.

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