

Synthesis and properties of Eu^{3+} -doped strontium fluoroapatite nanocrystals by low-temperature hydrothermal method

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A novel of Eu^{3+} -doped strontium fluoroapatite nanocrystals (Eu^{3+} : $\text{Sr}_{10}(\text{PO}_4)_6\text{F}_2$ or Eu^{3+} :S-FAP) were firstly prepared by a low-temperature hydrothermal method, using ethylenediaminetetraacetic acid disodium ($\text{Na}_2\text{H}_2\text{EDTA}$) as capping agent. Their morphology and structure were characterized by TEM, XRD and FTIR spectra. The results revealed that the nanocrystals mainly took on spherical-like shape and were well crystalline with an average diameter of less than 80 nm. Photoluminescence spectra indicated that the nanocrystals had high luminescence intensity ratio (R/O) of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions and high quenching concentration. They are promising materials for the applications of laser, display, and sensors.

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1. Introduction

Strontium fluoroapatite single crystals ($\text{Sr}_{10}(\text{PO}_4)_6\text{F}_2$ or S-FAP) can be used as good optical host for doping rare earth ions due to their widely application in the field of high efficient luminescent materials and novel laser media[1-3]. Among the unique features of fluoroapatites, relative to other hosts such as YAG, are the large induced crystal field splitting and high emission and absorption cross sections for optically active dopant ions. In addition, fluoroapatites are representative of larger family of compounds having the apatite structure; the study for the structure and properties could provide insights for investigating and developing other novel host materials for optical applications.

So far, S-FAP single crystals doped with Yb^{3+} ions have been found to exhibit highly favorable spectroscopic properties as laser media[4]. There are also some studies of Eu^{3+} :S-FAP powders which are of interest in the phosphor industry[5]. However, most of these doped fluoroapatites are prepared at high temperature (about 1000°C) in a solid-state reaction, or with at least one stage at high temperature. Few of them focused on nanosized Eu^{3+} -doped fluoroapatites by a low-temperature hydrothermal method with low cost. Therefore, it is significant to investigate the synthesis, structure and properties of rare-earth ions doped fluoroapatite nanocrystals by low-temperature method.

The crystal structures of S-FAP are well known in the literature[4]. The lattices are uniaxial and belong to the crystallographic group $\text{P6}_3/\text{m}$, two inequivalent cations (SrI and SrII) sites are present. Thereinto, SrI is coordinated by oxygen ions attached to phosphate groups and has C_3 symmetry; SrII is coordinated by oxygen ions and one

fluoride ion, and has C_s symmetry. According to literature reported[6], emission from Eu^{3+} in SrII sites at the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition appears with prominent features, due to the highly symmetric seven coordination. Several papers have reported the Eu^{3+} luminescence in fluoroapatites by solid phase method[4,7].

In this paper, a series of Eu^{3+} -doped S-FAP nanocrystals were firstly synthesized by hydrothermal method. This method achieves a low-temperature, mass-production, high-yielding, high fluorine content and economical route. The nanocrystals had well crystalline and good monodispersity. Moreover, high luminescence intensity ratio (R/O) of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions values and high quenching concentration were also found.

2. Experimental

2.1 Preparation of Eu :S-FAP nanocrystals

To synthesize Eu^{3+} :S-FAP nanocrystals, $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Na_2HPO_4 and NaF were used as starting materials. Ethylenediaminetetraacetic acid disodium salt ($\text{Na}_2\text{H}_2\text{EDTA}$) was used as additives. All chemicals were of analytical grade. Aqueous solutions were prepared by dissolving them into deionized water. A typical procedure was as follows: the appropriate amount of $\text{Sr}(\text{NO}_3)_2$ (1.152g, 5.4mmol) and $\text{Eu}(\text{NO}_3)_3$ (0.02453g, 0.1mmol), with an additive were added into a flask, followed by addition of desired amount of Na_2HPO_4 (0.436g, 3.3mmol) and NaF (0.055g, 1.1mmol) solution under stirring. Aqueous solutions were mixed together at a molar ratio of (Sr+Eu): Na_2HPO_4 :NaF = 5:3:1,

and stirred for 3min. The final pH value of the solution was controlled at 6. The obtained suspension was poured into a stainless Teflon-lined autoclave maintained at 110 °C for 10 h. The reaction system was then cooled down to room temperature. The resultant product was filtered, washed with distilled water and ethanol, and dried in oven at 70°C overnight.

2.2 Measurements

The transmission electron microscopy (TEM) image was taken on a Hitachi H-600 transmission electron microscope under a working voltage of 80kV. The XRD patterns of the samples were characterized by X-ray powder diffraction instrument with Cu K α 1/40 kV/100 mA. The Fourier Transform Infrared (FTIR) spectrum was carried out by Shimadzu TR prestige-21 FTIR Spectrometer. Photoluminescence (PL) spectrum was performed using Edinburgh Instruments FLS920 fluorescence spectrophotometer.

3. Results and discussion

3.1 TEM , XRD and FTIR analysis

The TEM micrograph of Eu³⁺(1mol%):S-FAP nanocrystals is shown in Fig. 1. It can be seen that the nanocrystals mainly bear spherical-like shape and the primary particle sizes are less than 80nm. It reveals that spherical-like primary Eu³⁺:S-FAP nanocrystals are formed under the present experimental conditions. Furthermore, some short-rod like nanocrystals were also found. This can be explained by particle growth mechanism in Eu³⁺-Sr²⁺-F⁻-PO₄³⁻-H₂O precipitating systems. The growth of Eu:S-FAP nanocrystals results preferentially from the aggregation of smaller precursor units[8].

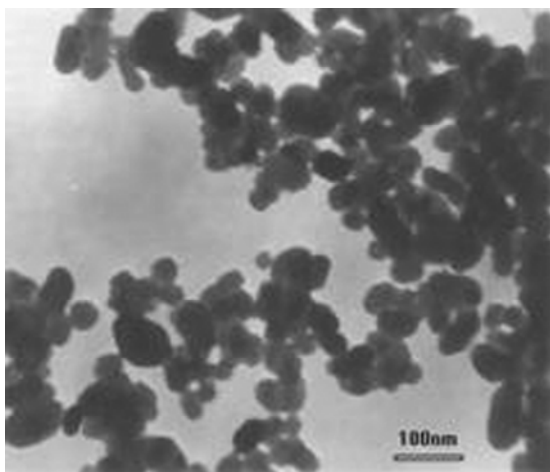


Fig. 1. TEM image of Eu³⁺:S-FAP nanocrystals.

Fig. 2 is the FTIR spectra of Eu³⁺(1mol%):S-FAP

nanocrystals mixed with spectroscopic grade KBr. It shows that the stretching and bending vibration of P-O bonds in phosphate group remained in the positions of 1093, 1045, 947, 595, and 563 cm⁻¹. The peak at 1664 cm⁻¹ and the broad band at 3450 cm⁻¹ are assigned to bending mode of H₂O molecules, which show that OH⁻ may incorporate into strontium fluoroapatite to form the hydroxy/fluoroapatite solid solution. The band at 1602cm⁻¹ is the character of carboxyl stretching vibration, which implies EDTA-Na₂ molecules are absorbed on the surface of nanocrystals. The nanocrystals strong aggregation is effectively inhibited because of the presence of EDTA-Na₂ molecules.

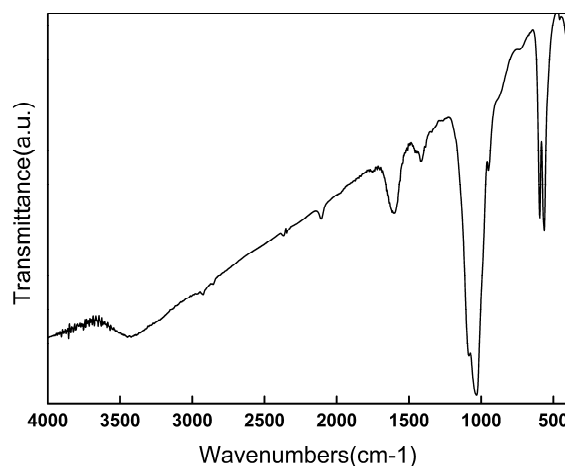


Fig.2. FTIR spectra of Eu³⁺:S-FAP nanocrystals

The XRD patterns of Eu³⁺:S-FAP nanocrystals with different Eu³⁺ concentration are shown in Fig.3. They match well with the standard pattern of No.17-609 and the peaks indexed base on hexagonal crystal structure. It is worthwhile noting that good crystallization is already obtained by low-temperature hydrothermal method. For Eu³⁺(1mol%):S-FAP sample, the calculated lattice parameters are a=9.73Å, c=7.29Å, which are similar to the reported parameters of S-FAP(a=9.71Å, c=7.28Å) by coprecipitation method[9]. The crystallite size was estimated from the X-ray diffractograms using the Scherrer formula

$$D = K\lambda/\beta\cos\theta \quad (1)$$

where D is the crystallite size (Å) perpendicular to (002) plane, K is a shape factor equal to 0.89, λ is the X-ray wavelength (1.5405 Å), θ is the diffraction angle related to the reflection 002 ($\theta = 12.2305^\circ$), and β is full width at half maximum of the diffraction peaks. By applying the Scherrer formula to the full width at half maximum of the diffraction peaks, we could calculate the average particle sizes of Eu³⁺ (1mol%):S-FAP as 70 nm, which is consistent with the average particle scales deduced from

TEM. From Fig. 3, it could also be seen that the interplanar distances slightly shift, indicating crystal lattice occurred different distorted with different dopant concentration [10]. When the Eu^{3+} dopant concentration reaches 10mol %, the diffraction peak intensity decreases significantly, which show the lattice is seriously distorted.

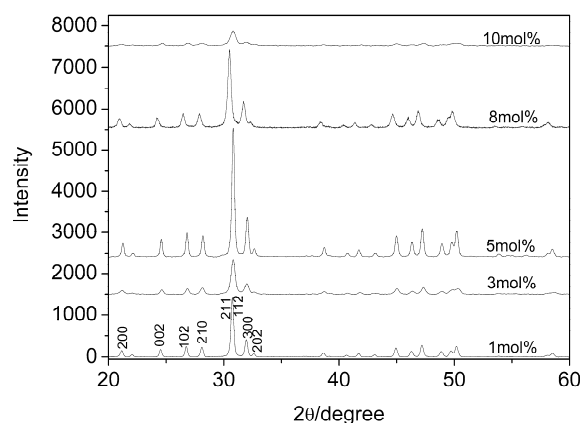


Fig. 3. XRD patterns of Eu^{3+} :S-FAP nanocrystals with different Eu^{3+} concentration

3.2 Fluorescence properties

Fig. 4 shows the fluorescence spectra of Eu^{3+} :S-FAP nanocrystals with a various of Eu^{3+} concentration for excitation at 395nm. All of these are attributed to the emission of different Eu^{3+} sites in the apatite lattice. The main peaks located in 591–594, 614–616 nm ranges and 700 nm correspond to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions of Eu^{3+} , respectively

The intensity of the enforced electric-dipole-allowed $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition depends strongly on Eu^{3+} surroundings. Therefore, the luminescence intensity ratio (R/O) of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions, widely known as the asymmetric ratio, provides valuable information about the symmetry at the site of Eu^{3+} in the host matrix[9,11]. As shown in Table1, the R/O values of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions are about between 2.70 and 2.85, which show more Eu^{3+} may occupy SrII sites. Moreover, take 5mol% Eu^{3+} for example, the R/O value was estimated about 2.4 and it can be seen that the R/O value is higher in nanocrystals than in the bulk materials[12]. The intensity enhancement of this hypersensitive transition in nanocrystals could be explained by a dynamical coupling model [1]. Because the surfaces of nanocrystals have more defects and distorted lattice. It can reduce the local symmetry of Eu^{3+} ions in nanocrystals and increase R/O value in nanosized Eu :S-FAP samples.

In addition, it is found that when Eu^{3+} doping concentration reaches 8 mol%, luminescence intensity becomes lower. That is to say, concentration quenching

effect occurs. In nanosized materials, resonance energy transfer only occurs within one particle due to the hindrance by the particle boundary. Therefore, nanocrystals can obtain higher quenching concentration [10].

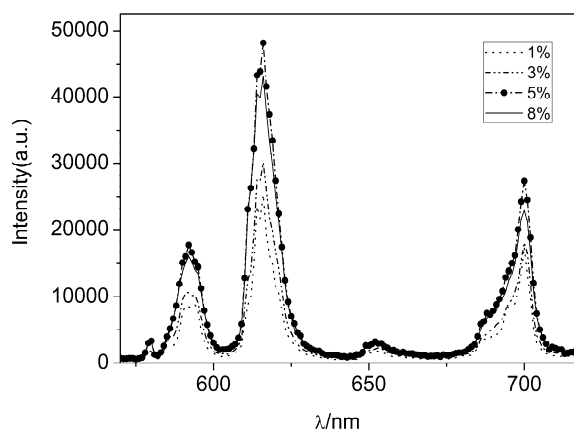


Fig. 4. Fluorescence spectra of Eu^{3+} :S-FAP nanocrystals with a various of Eu^{3+} concentration.

Table 1. Intensities and R/O ratios of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition of Eu^{3+} :S-FAP nanocrystals with different dopant concentration.

Eu^{3+} concentration	$^5\text{D}_0 \rightarrow ^7\text{F}_2$ intensity	$^5\text{D}_0 \rightarrow ^7\text{F}_1$ intensity	R/O values
1mol%	24731	8743	2.83
3mol%	29905	10874	2.75
5mol%	48154	17624	2.73
5mol% (bulk)	—	—	2.4
8mol%	43005	15594	2.75

4. Conclusions

A novel of Eu^{3+} -doped strontium fluoroapatite nanocrystals with average diameter of less than 80nm, were firstly prepared and characterized in detail. The fluorescence properties of the nanocrystals with different dopant concentration were also studied at room temperature. High fluorescent intensity ratio(R/O) and high quenching concentration in Eu^{3+} :S-FAP nanocrystals were obtained.

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