



Preparation and optical properties of SrF₂:Eu³⁺ nanospheres

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ABSTRACT

SrF₂:Eu³⁺ nanospheres with homogeneous diameter have been synthesized by a microemulsion-mediated hydrothermal method for the first time, in which quaternary microemulsion of CTAB/water/cyclohexane/*n*-pentanol was used. The possible reaction mechanism and the luminescent properties of SrF₂:Eu³⁺ nanospheres were also investigated in this paper. The morphology and grain sizes of final products were characterized by field emission scanning electron microscopy and transmission electron microscopy, indicating that most of the products were nanospheres with an average diameter of ~50 nm. Room-temperature emission spectra, recorded under 394-nm excitation, showed that the transition of ⁵D₀ → ⁷F₁ emission be dominating in SrF₂:Eu³⁺ nanospheres. From the dependence of the luminescence intensity on the concentration of Eu³⁺ ions, the optimal dopant concentration is 2 mol%.

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1. Introduction

Fluorides have wide applications in optics as windows, lenses, scintillation crystals [1], and they are also as host crystals for rare earth ions (Ho, Er, Eu, Nd, Ce) exhibiting interesting properties in optoelectronics such as lasing [2], light amplification, and upconversion [3–5], alkaline-earth fluorides, such as CaF₂, SrF₂, and BaF₂ in cubic fluorite structure, constitute an important class of relatively simple ionic crystals, whose optical and lattice-dynamical properties are of much theoretical and experimental interest [6,7]. For instance, Falin et al. [8] reported optical spectroscopy of Yb³⁺ ions in CaF₂ and SrF₂. Bouffard et al. [4] showed red-to-blue upconversion spectroscopy of Tm³⁺ in SrF₂, CaF₂, BaF₂, and CdF₂.

Many efforts have generally focused on bulk alkaline-earth fluorides and other nanomaterials, such as carbon nanotubes, quantum dots, metallic nanoparticles, and metal oxide nanostructures, however, the preparation of low-dimensional alkaline-earth metal fluorides, including barium fluoride, strontium fluoride, and calcium fluoride, is at a nascent stage [9–15]. In 2000, Bender et al. [12] reported the synthesis of BaF₂:Nd³⁺ nanoparticles the reverse microemulsion technique. Three years later, Cao et al. [11] synthesized one-dimensional fluoride nanostructures—BaF₂ whiskers by a microemulsion-mediated

hydrothermal method. Sun and Li [10] synthesized single crystal CaF₂ nanocubes by a simple hydrothermal method. Now, some workgroups have made some efforts on the synthesis of nanostructured EuF₃ [15] and other LnF₃ (Ln = La, Gd) [16–18], however, to the best of our knowledge no experimental study regarding on the homogeneous morphology strontium fluoride nanospheres has been reported up to now. In this letter, we have investigated the preparation of europium-ion-doped SrF₂ nanospheres and their photoluminescence properties.

2. Experimental

All the starting materials were of analytical grade and they were used as received from the supplier without further purification. In the experiment, a quaternary microemulsion, CTAB/water/cyclohexane/*n*-pentanol, was select. First, two identical transparent solutions were prepared by dissolving appropriate CTAB in a mixture of cyclohexane (6 mL) and *n*-pentanol (0.5 mL). A solution of SrCl₂ with EuCl₃ and a 40% HF solution (1 mL) were dropped into the solutions of CTAB, cyclohexane and *n*-pentanol, respectively, with vigorous stirring over 30 min at 30 °C. Thereafter, the two optically transparent microemulsion solutions were mixed together and the precursor microemulsion solution was obtained. It was transferred into a 25-mL stainless Teflon-lined autoclave subsequently and the autoclave was kept at 130 °C for 12 h. It was allowed to cool down to room temperature naturally, and the resulting suspension was stored at a constant temperature of 35 °C for 24 h. Following that, the product was collected and was washed several times with absolute ethanol and distilled water. Finally, the

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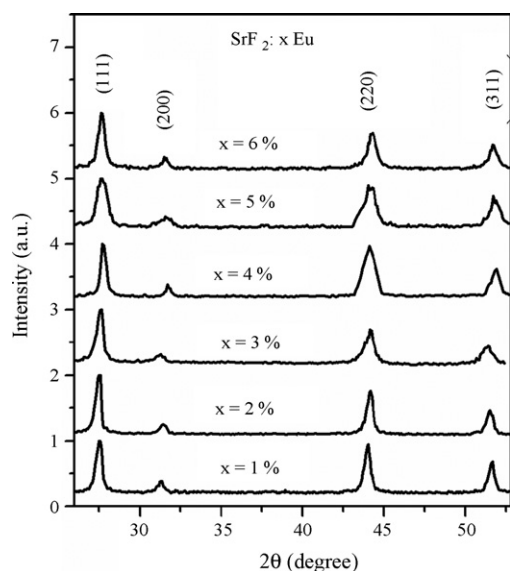


Fig. 1. XRD patterns of SrF₂ nanospheres with different Eu³⁺ concentrations.

result dispersion was centrifuged and dried in vacuum at room temperature. The white powder was obtained and the production quantity is about 0.4 mg SrF₂ mL⁻¹ reaction solution.

The structures of samples were characterized by X-ray diffraction (XRD) (Rigaku D/max-rA powder diffractometer with Cu target radiation resource ($\lambda = 1.54078 \text{ \AA}$)); the morphology and size were investigated by using field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Excitation and emission spectra were recorded at room temperature using a fluorescence spectrometer (Hitachi F-4500) with a 2.5-nm bandpass.

3. Results and discussion

The XRD patterns of SrF₂ nanospheres with different Eu³⁺ concentrations are shown in Fig. 1, and all of the diffraction peaks can be readily indexed to a pure cubic phase (space group: *Fm* $\bar{3}$ *m* (2 2 5)), which are in agreement with the standard values for cubic SrF₂ (JCPDS no. 86-2418) basically. No signals of Eu³⁺ were observed in the synthesized product owing to the low dopant concentration. The XRD results indicate that the products we obtained were SrF₂ nanoparticles. Hall's plots of SrF₂:3% Eu³⁺ as an example is shown in Fig. 2 and the lattice distortion can be obtained from the slope. For this sample, the distortion is 11.75% that is the biggest one in all of

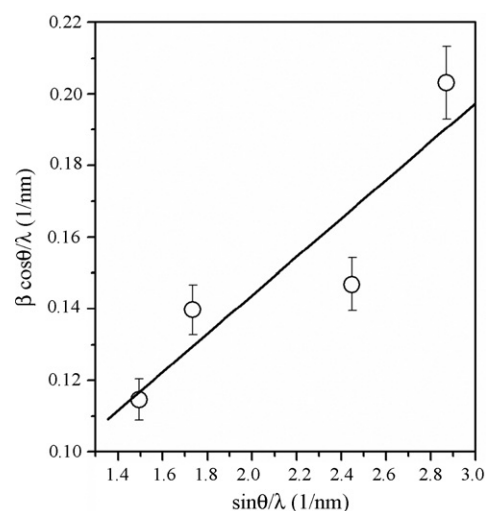


Fig. 2. Hall's plots of nanospheres SrF₂:3% Eu³⁺.

our products. When the concentrations of Eu³⁺ ions are 1 and 6%, the distortions are 2.3 and 1.4%, respectively. That is to say, here, the dopant concentration does not relate to the distortion.

Fig. 3 depicts that the morphology of the as-synthesized product is about 50-nm nanospheres. Fig. 3a is a wide-field SEM image of the as-prepared SrF₂:2% Eu³⁺ nanospheres, displaying that the products are composed of some homogeneous nanospheres with an average diameter about 50 nm. From SEM image of the sample, a distribution of nanospheric diameter was statistic, as shown in Fig. 4. The distribution of the nanospheric diameter is around 50 nm and the mean diameter is ~50.3 nm from Gaussian fit. Gaussian fit shows the clear tendency of diameter's distribution. More details about the product were investigated by TEM analysis (Fig. 3b) and the select area electronic diffraction (SAED) pattern (the inset). The sample for TEM characterization was prepared by placing a droplet of solution on a carbon-coated copper grid and letting it air-dry. TEM image shows the opaque nanosphere with clear outline on the copper grid. Moreover, the SEAD pattern displays SrF₂:Eu³⁺ is single crystal, which is taken from some single nanosphere. The energy-disperse X-ray (EDX) spectrum (see Fig. 5) taken from a single nanosphere further affirms the formation of SrF₂ phase and the percentage of Eu. The sample is SrF₂:5 mol% Eu³⁺ and the percentage of Eu³⁺ calculated by the computer is 2.56%.

In the experiment, CTAB is a surfactant in the water/oil microemulsion and the possible mechanism of the SrF₂:Eu³⁺ nanospheric formation is shown in Fig. 6. It was carried out

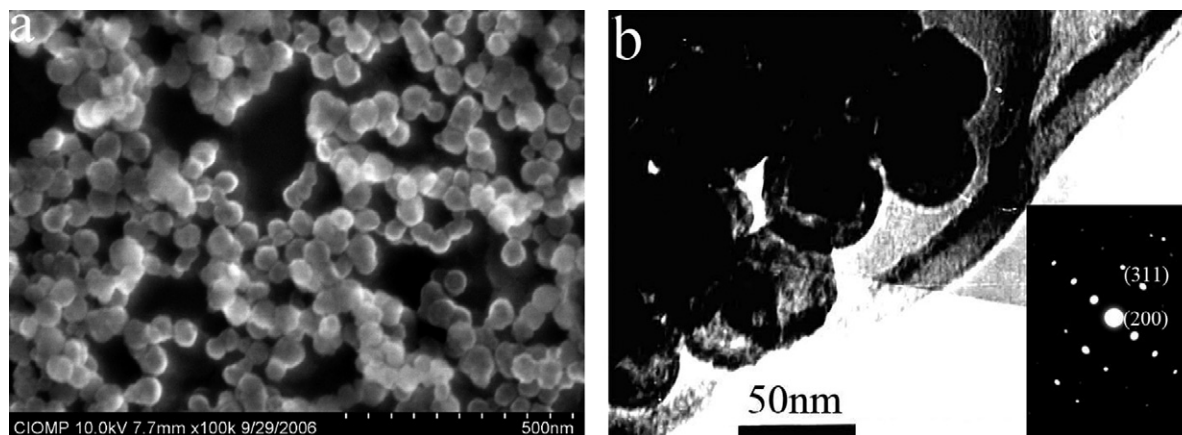


Fig. 3. (a) SEM image of SrF₂:Eu³⁺ nanospheres; (b) TEM image of SrF₂:Eu³⁺ nanospheres; inset: select area electron diffractions (SAEDs) recorded on individual nanospheres.

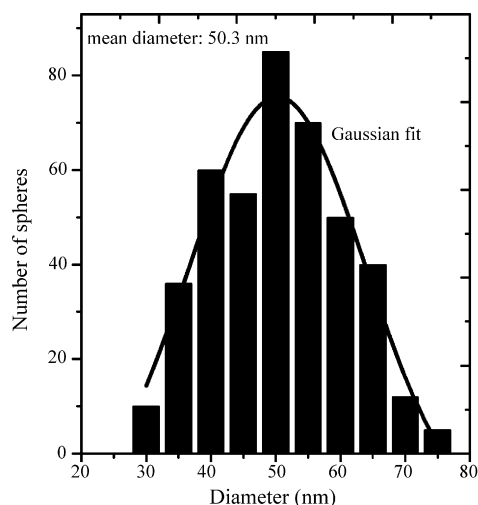


Fig. 4. Histogram of the particle size distribution obtained from SEM images (Fig. 2a).

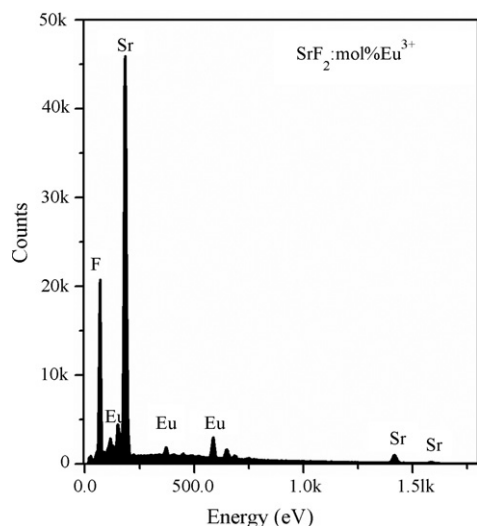


Fig. 5. Representative EDX spectrum of a single nanosphere of SrF₂:5 mol% Eu³⁺.

through three steps as follows: (1) the formation of the microemulsion drop. The surfactant often has hydrophilic group and hydrophobic group. CTAB is solved in the mixed solution of cyclohexane and *n*-pentanol, and the microemulsion environment begins to be set up. (2) After the hydrophilic hydrophobic balance, the formation of precipitation of SrF₂:Eu³⁺ in the microemulsion drop. (3) The formation of SrF₂:Eu³⁺ nanospheres. The microemulsion drop is like a very small reaction vessel that limits the growing up of the particles.

Room-temperature emission spectra of SrF₂ with different Eu³⁺ concentrations have been investigated, which is shown in Fig. 7. Some emission lines have been observed in the emission spectrum,

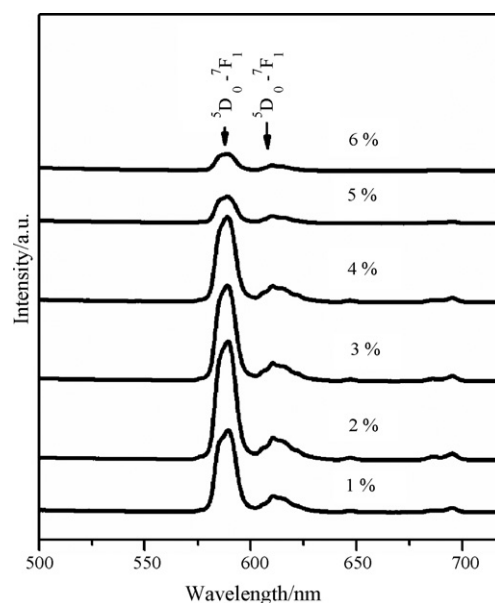


Fig. 7. Room-temperature emission spectra of SrF₂:Eu³⁺ nanospheres ($\lambda_{\text{ex}} = 394 \text{ nm}$) with different Eu³⁺ concentrations.

which are associated with the transitions of Eu³⁺ ions from the ⁵D₀ level to ⁷F_{*J*} (*J* = 0, 1, 2, 3, 4) levels. The emission of ⁵D₀ → ⁷F₀ transition can be observed only when Eu³⁺ ions locate in low symmetric sites. The ⁵D₀ → ⁷F₁ transition is parity-allowed magnetic dipole transition, which is slightly affected by the symmetry of the Eu³⁺ site. The ⁵D₀ → ⁷F₂ transition is a parity-forbidden electric dipole transition and the probability of its transition is very sensitive to relatively small changes of the environment around Eu³⁺ ions. Its strong emission only occurs in non-inversion symmetry sites. So the Eu³⁺ ion is often occupied as a probe to detect the surroundings of the matrix. In the spectra, the ⁵D₀ → ⁷F₁ transition is much stronger than others and the ⁵D₀ → ⁷F₀, ⁵D₀ → ⁷F₃, ⁵D₀ → ⁷F₄ transitions are hardly observed. Moreover, the emission intensity is related to the dopant concentration of Eu³⁺ ions. In Fig. 8, it shows the dependence of the integrated luminescence intensity of SrF₂:Eu³⁺ nanospheres on the concentration of Eu³⁺ ion dopant by monitoring the emission of ⁵D₀ → ⁷F₁ transition at 590 nm, which was calculated from Fig. 6. The luminescence intensity was enhanced with the increasing Eu³⁺ concentration when it lower than 2 mol% and it reached to the maximum at 2 mol% of Eu³⁺ ions. For higher Eu³⁺ concentration, there is a significant decrease of the luminescence intensity. So for Eu³⁺-doped SrF₂, the quenching concentration is about 2 mol%. The decrease of the integrated luminescence intensity of SrF₂:Eu³⁺ on the concentration of Eu³⁺ ion dopant is affected by two main points. One is the distortion of the lattice caused by the high doping; the other is energy dispersion between Eu³⁺ ions. The effect of the distortion of the lattice caused by the high doping to the luminescence has been excluded in the forgoing Fig. 2. The concentration quenching should be attributed to the non-radiative

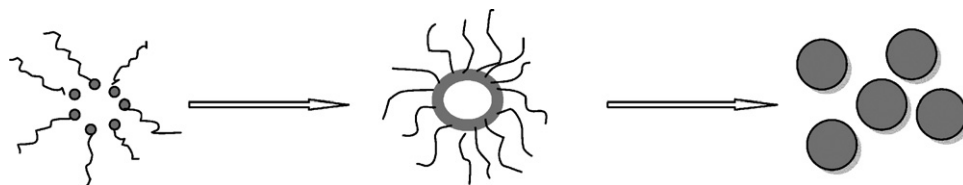


Fig. 6. A schematic diagram of the formation mechanism of the spherical SrF₂:Eu³⁺ nanocrystal.

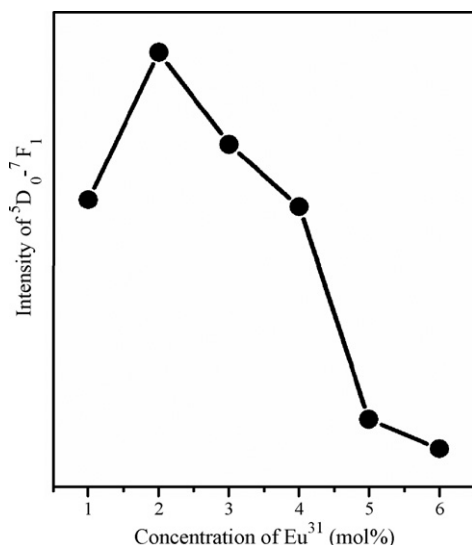


Fig. 8. Luminescent intensity of SrF₂:Eu³⁺ depending on Eu³⁺ concentration.

transfer resulted from resonance energy transfer between adjacent europium (III) ions which was publicly studied by the researchers [19,20].

The quantum yield of SrF₂:2 mol% Eu³⁺ is 2.5%. PL quantum yields of SrF₂:Eu³⁺ ethanol solution were measured by comparing the integrated emission of an ethanol solution of Rhodamin 6G (laser grade; quantum yield 95%) under 394-nm excitation.

4. Conclusions

In conclusion, the current report describes the synthesis of pure phase SrF₂:Eu³⁺ nanospheres in uniform diameter of ~50 nm by quaternary microemulsion-mediated hydrothermal method. It is noteworthy that the quaternary microemulsion-mediated hydrothermal method is effective for obtained pure phase nanomaterials

with controllable size, uniform morphology and shape. Resulting nanospheres have been characterized using spectroscopy data. From the dependence of the luminescence intensity on the concentration of Eu³⁺, the optimal concentration of dopant Eu³⁺ ions for SrF₂ nanosphere was about 2 mol%. The synthesis and the luminescence properties of SrF₂:Eu³⁺ nanospheres provide a basis for our more thorough investigation of further optical and optoelectronic properties into nanoscale devices.

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