

Systematic investigations into SrSnO₃ nanocrystals (II) photoluminescent properties of the as-synthesized nanocrystals

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Abstract

The luminescence properties of Eu³⁺-doped SrSnO₃ nanocrystals, synthesized by combustion and coprecipitation methods, were investigated. The different synthesized methods make the valence of the doped ion and the crystallinity of the as-synthesized nanocrystals different, resulting in the difference of the amount, site and intensity of the emission peaks.

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1. Introduction

Recently, considerable interest in the novel optical and electrical properties of doped nanoparticles has emerged. Alternative classes of these materials that exhibit unique optical properties are those based on oxides doped rare earth ions [1,2]. Lanthanide luminescent probes are being increasingly used to solve a variety of structural and analytical problems [3]. The Eu³⁺ ion exhibits two main advantage: first, because of its simple and well-documented luminescence scheme, it serves as a very efficient and sensitive structural probe [4] and second, its luminescence, in the case of a non-centrosymmetric environment, is generally dominated by the ⁵D₀ → ⁷F₂ transition yielding a red emitting phosphor suitable for lamps and displays [5].

In view of the information gaps in the reported research among important parameters, such as, synthesis, processing, microstructure and the correlative behaviors of strontium stannate (SrSnO₃) and lack of data on the photoluminescent properties envisaged in these materials, systematic investigation has been carried out step by step in our study.

2. Experiment

The synthesis progress has been discussed in the first part of the systematic investigations. Here, the simple progress will be described. All reagents

were analytical reagent grade and used without any further purification. Stannic chloride pentahydrate (SnCl₄·5H₂O) and strontium nitrate [Sr(NO₃)₂] with Eu³⁺ ions molar ratio from 3 to 7 mol% were dissolved in a minimum amount of distilled water. The mixture of the two solution with a Sr:Sn molar ratio of 2.5:1 was added dropwise into ammonia (NH₃·H₂O) aqueous solution (V_{NH₃·H₂O} : V_{H₂O} = 1 : 4) under magnetic stirring. The final mixture was alkaline with a pH value around 9 to ensure the complete reaction of the reagents. The as-synthesized precipitation was filtered and washed with distilled water to remove undesirable anions such as Cl⁻ and NO₃⁻. Then the precursor called hereafter, was stirred in a solution, consisting of ammonium nitrate (NH₄NO₃) and urea [CO(NH₂)₂], and heated at 100 °C to minimize the amount of water. Finally, a crucible containing the reagent mixture was placed in an oven kept at 600 °C for 10 min to obtain the Eu³⁺-doped SrSnO₃ nanocrystals. The corresponding nanocrystals were synthesized by coprecipitation after the precursor dried in an air atmosphere at 120 °C for 2.5 h, and then calcined in an oven at 1000 °C for 1 h.

The photoluminescence properties of the powders were measured with a Hitachi 850 fluorescence spectrometer.

3. Results and discussion

In the view of Riwotzki and Haase [6], a part of the energy level diagram of the Eu³⁺ ion in a solid host is shown in Fig. 1. Only energy levels are given which are involved in transitions observed in the luminescence spectrum. The ⁷F₀ level is the highest level occupied (at 0 K). Many more levels are known at energies higher than the ⁵D₀ level. While the overall energy level structure of the Eu³⁺ ion does not change in the different hosts due to the shielding of the 4f electrons by outer shell 5s and 6p electrons, each energy level shown in the figure can be split up into 2J + 1 sublevels by the local crystal field surrounding the

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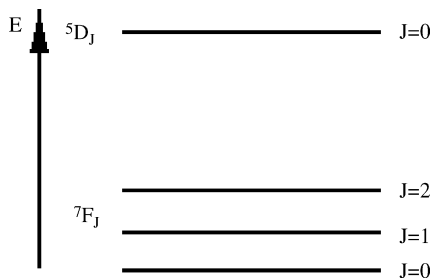


Fig. 1. Part of the energy level diagram of the Eu^{3+} ion.

Eu^{3+} ion. In fact, the lines observed in the luminescence spectrum correspond to transitions between sublevels of the energy levels shown in the figure.

The intensity of transitions between different J -number levels depends on the symmetry of the local environment of the europium ion and can be described in terms of the Judd-Ofelt theory, which states that magnetic-dipole transitions are allowed if $|\Delta J|=0$ or 1 (but not $J=0 \rightarrow J'=0$), regardless of environment [6]. On the other hand, the $\text{Eu}^{3+} 5D_0 \rightarrow 7F_2$ emission belongs to a hypersensitive transition with $|\Delta J|=2$, which is strongly influenced by the local environment. When the Eu^{3+} ion is located at a low-symmetry local site (without an inversion center), this emission transition often dominates in its emission spectrum [7].

The luminescence spectrum and the emission intensity curves of 7 mol% Eu^{3+} -doped SrSnO_3 synthesized by combustion method are displayed in Fig. 2. The most intense transitions observed in the luminescence spectrum originate from the $5D_0$ level, which is not split by the crystal field ($J=0$). When excited at 257 nm, all luminescence lines can correspond to the characteristic transitions from $5D_0$ to $7F_J$ ($J=0, 1, 2$) states at around 600, 595 and 615.5 nm, respectively. Although either the hypersensitive $5D_0 \rightarrow 7F_2$ transition (Eu^{3+} site without inversion symmetry), not the magnetic-dipole allowed $5D_0 \rightarrow 7F_1$ transition (Eu^{3+} site with inversion symmetry) can dominate transition of Eu^{3+} in the SrSnO_3 host synthesized by combustion method, no site symmetry is known where the $5D_0 \rightarrow 7F_0$ transition has the highest intensity in the spectrum. On the other hand, the emission intensity of the $5D_0 \rightarrow 7F_0$ transition does not change obviously with the change of the doped concentration (seen from Fig. 2b) for the nanocrystals synthesized by combustion method, and disappears absolutely for the doped nanocrystals synthesized by coprecipitation method (Fig. 3a). Therefore, it is unlikely that the yellow emission at 565 nm here is caused by the $5D_0 \rightarrow 7F_0$ transition of Eu^{3+} in a different site. A more likely explanation is that this emission is caused by Eu^{2+} according to the former reports [8,9]. The fact that Sr^{2+} and Eu^{2+} ions have very close ionic radii explains why Eu^{3+} ions introduced in the Sr^{2+} sites of SrSnO_3 are easily reduced to Eu^{2+} , which accords well with the experimental result of Clabau et al. [10]. The emission intensity at 565 nm does not change obviously as seen from Fig. 2b can be attributed to that the emission intensity of Eu^{2+} can hardly change because the luminescence of Eu^{2+} mainly relies on the coordination number, covalency and crystal field strength at Eu^{2+} site [11]. The existence of Eu^{3+} emission may be caused by the fact that part of Eu^{2+} is oxi-

dized to Eu^{3+} in ambient atmosphere. It is interesting to find from Fig. 2b that the $5D_0 \rightarrow 7F_1$ transition emission has a sharp increase and decrease before and after the doped concentration of 4 mol%. The emission intensity is even higher than that of the $5D_0 \rightarrow 7F_0$ transition emission. The exact mechanism for this phenomenon to occur is still not yet clear. The decrease of the emission intensity is caused by the concentration quenching after the activator concentration increases above the optimum concentration, i.e. 4 mol% Eu^{3+} .

The luminescence spectrum and the emission intensity curves of 7 mol% Eu^{3+} -doped SrSnO_3 synthesized by coprecipitation method are displayed in Fig. 3. When excited at 257 nm, all luminescence lines correspond to the characteristic transitions from $5D_0$ to $7F_J$ ($J=1, 2$) states at around 600 and 624.5 nm, respectively. The emission spectrum of the nanocrystals synthesized by combustion method has a relative blue-shift, which can be attributed to the small particle size of the as-synthesized nanocrystals. The phenomenon that the 565-nm emission disappears in the emission spectrum of the nanocrystals synthesized by combustion method due to these processes, Eu^{2+} is oxidized to Eu^{3+} , while residual Eu^{3+} is reduced to Eu^{2+} with difficulty when the nanocrystals are obtained by 1000 °C heating for 1 h in ambient atmosphere. It can be observed from Fig. 3a that the magnetic-dipole $5D_0 \rightarrow 7F_1$ transition (Eu^{3+} site with inversion symmetry), not the hypersensitive $5D_0 \rightarrow 7F_2$ transition

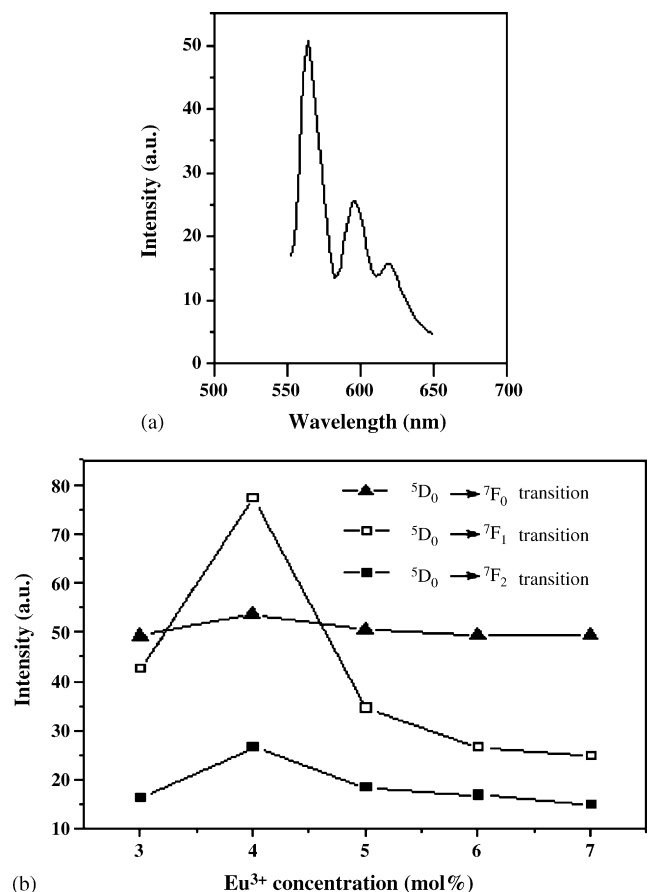


Fig. 2. Luminescence spectrum (a) and the intensity curves (b) of 7 mol% Eu^{3+} -doped SrSnO_3 synthesized by combustion method.

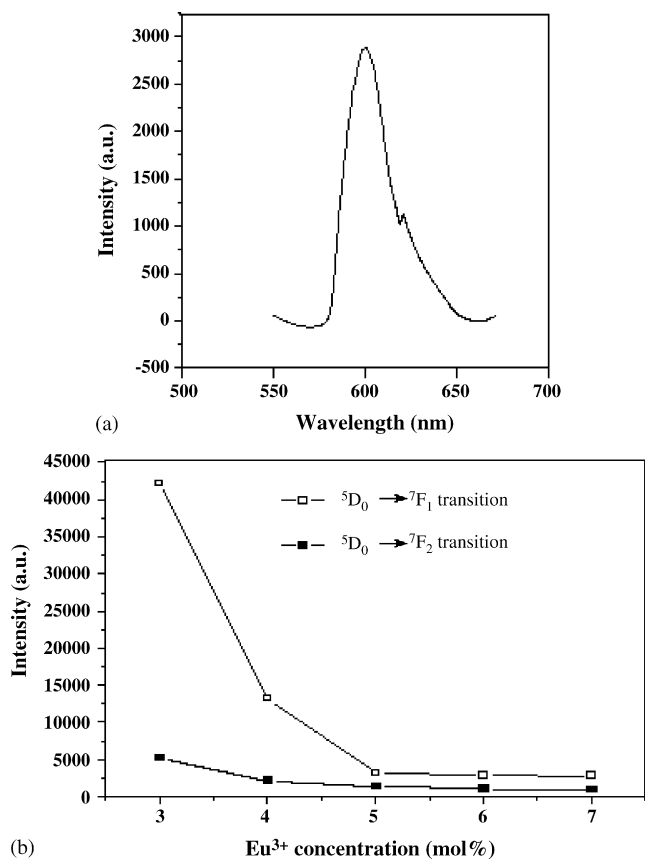


Fig. 3. Luminescence spectrum (a) and the intensity curves (b) of 7 mol% Eu^{3+} -doped SrSnO_3 synthesized by coprecipitation method.

(Eu^{3+} site without inversion symmetry), dominates in the emission spectrum of the nanocrystals synthesized by coprecipitation method. The ${}^5D_0 \rightarrow {}^7F_2$ transition emission decreases slowly all the while, whereas the ${}^5D_0 \rightarrow {}^7F_1$ transition emission has a sharp decrease when the doped concentration increases from 3 to 4 mol%. It can be seen that there is a great increase in the emission intensity of the nanocrystals synthesized by coprecipitation method comparing with those synthesized by combustion method within all the studied concentrations of Eu^{3+} ion since the emission intensity of the as-synthesized nanocrystals is measured with the same measurement scale. This phenomenon may result from the nanocrystals crystallinity increasing with the increase of annealing temperature. The quenching of the luminescence of the Eu^{3+} ion by the vibrations of the defects decreases, resulting in the increase of the emission intensity.

There are two cation places for Eu^{3+} to replace, i.e. Sr^{2+} and Sn^{4+} ions. The potential energy of an ion is similar in the different ion lattice, i.e. its contribution to the lattice energy is similar. This contribution is so-called energy coefficient. The energy coefficient of the high-valence ion is higher than that of the low-valence ion. The lattice energy will increase after the high-valence ion replaces the low-valence ion, which makes the crystal more stable. On the contrary, the lattice energy and the stability of the crystal will decrease after the low-valence ion

replaces the high-valence ion. Thus, it is difficult for this contrary process to occur. Thereby, it is reasonable to conclude that the Eu^{3+} ion is located at the Sr^{2+} site in a Sn-O cube in structure with an $\bar{4}$ axis. The local charge balance can be maintained by the creation of one strontium vacancy (V_{Sr}) for every two Eu^{3+} ions substituting for every three Sr^{2+} ions. The existence of the $\bar{4}$ axis makes the magnetic-dipole ${}^5D_0 \rightarrow {}^7F_1$ transition (Eu^{3+} site with inversion symmetry), not the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition (Eu^{3+} site without inversion symmetry), dominant in the emission spectrum.

4. Conclusion

A strong luminescence emission occurs in the doped nanocrystals synthesized by combustion method because Eu^{3+} ions introduced in the Sr^{2+} sites of SrSnO_3 are easily reduced to Eu^{2+} with the instantaneous reaction at a low temperature. On the other hand, Eu^{2+} is oxidized to Eu^{3+} , while residual Eu^{3+} is reduced to Eu^{2+} difficultly when the nanocrystals obtained by coprecipitation method. Eu^{3+} ions, however, substitute Sr^{2+} , which makes the magnetic-dipole ${}^5D_0 \rightarrow {}^7F_1$ transition (Eu^{3+} site with inversion symmetry) dominant in the emission spectrum because of the existence of the $\bar{4}$ axis. With the increase of the reaction temperature, the crystallinity of the as-synthesized nanocrystals increases, resulting in a great increase in the emission intensity of the nanocrystals synthesized by coprecipitation method comparing with those synthesized by combustion method within all the studied concentrations of Eu^{3+} ion.

Acknowledgments

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