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Synthesis and luminescent properties of SnO_2:Eu nanopowder via polyacrylamide gel method

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Abstract

Nanocrystalline europium-doped tine oxide (SnO_2:Eu) were synthesized by a polyacrylamide gel method. The effects of heat treatment on structure, grain size and luminescence properties of SnO_2:Eu were studied with X-ray powder diffraction, transmission electron microscopy and photoluminescence measurements. The results indicate that high heat treatments can enhance greatly luminescence intensity of the samples. Furthermore, the presence of carbon network/cages in the polyacrylamide gel can effectively prevent particles agglomeration, so even when sintered at higher temperatures (1000 °C), the grain size is still below 20 nm.

Keywords: SnO_2:Eu; Nanocrystlline; Luminescence; Polyacrylamide gel method

1. Introduction

Recently, most research interests have been focused on rare-earth (RE) ions-doped semiconductors because of their potential applications in thin-film electroluminescent (TFEL) devices [1], cathodoluminescent devices [2]. Tin oxides (SnO_2), with a wide band gap (3.6 eV), is a very important *n*-type semiconductor. There has been a growing interest in luminescence of RE ions-doped SnO_2, such as SnO_2:Eu [3,4], SnO_2:Dy [5]. But due to the large difference of the radius and charge between RE ions and Sn^{4+}, it is difficult for RE ions to enter the lattice of SnO_2, which results in the poor luminescence of the phosphor.

With a motivation to resolve this problem, many investigations have been done on various synthesis routes of nanosized RE-doped SnO_2. Among them, the most common routes involve coprecipitation [3], sol–gel [4,5] and so forth. In these methods, starting from tin chlorides ($SnCl_4$ or $SnCl_2$) is generally preferred because they are easy to perform and the cost is very low [6], but the chlorine ions are very difficult to remove which can affect inevitably the luminescence of RE-doped SnO_2. In our paper, we adopted metal Sn as starting materials to prepare nanosized SnO_2:Eu. In this way, the effect of chloride ions can be eliminated. On the other hand, it is well known that the polyacrylamide sol–gel process was a fast, cheap, reproducible and easily scaled up chemical route for obtaining fine powders of composite oxide [7,8]. During the synthesis process, because the metal ions are completely dissolved in polymeric resin, the PG synthesis provides a molecular level mixing of elements [9–11], which helps the RE ions to incorporate into SnO_2.

In this paper, we will describe the properties of Eu-doped tin oxide nanocrystallines produced by polyacrylamide gel method. The concentration of Eu ions in the samples was kept constant at 1 mol% and this value was checked by chemical analysis. The properties of the powders were characterized and estimated by using X-ray diffraction (XRD), infrared absorption (IR) and photoluminescence (PL).

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2. Experimental section

2.1. Synthesis

The procedure used to prepare nanosized SnO_2:Eu is as follows. Firstly, 1.206 g of pure Sn (8 mmol) was dissolve in 20 mL cold dilute nitric acid (2 mol L^{-1}). In order to accelerate dissolution of Sn, 3.362 g citric acid (16 mmol) was added. The mixture were kept stirring for 2 h to obtain transparent yellow solutions. The final PH was controlled as 6–7 by using dilute ammonia. Subsequently, the monomers of acrylamide (3 g) and the cross-linker *N*,*N*-methylene-bisacrylamide (0.429 g) were added into the clear solution, in proportions indicated in Ref. [7]. The resulting solution was heated in a water bath and during the whole process, the system was continuously stirred. The solution became gradually transparent with temperature rising. When the temperature reached about 80 °C, a small amount of compound initiator AIBN ($C_8H_{12}N_4$) was added into the solution and polymerization occurred quickly and transparent polymeric resin was obtained without any precipitation. At last, the gel was dried at 100 °C for 24 h to yield a xerogel. The xerogel was heated in a laboratory furnace at 300 °C to burn out the organic residues and calcined at higher temperature (400–1000 °C) to obtain different samples.

2.2. Characterization

Phase purity and crystal structure of the obtained materials were determined by XRD. The measurements were obtained with a Rigaku D/MAX RB X-ray diffractometer using Cu*K*α radiation ($\lambda = 1.5418$ Å and $\theta = 20$–$65°$), at room temperature. Micrographs were recorded using JEM-2000Ex transmission electron microscope (TEM) under a working voltage of 100 kV. Specimens were prepared by dispersing small amounts of the powder in ethanol.

IR spectra were obtained on a JASCO FTIR 480 plus spectrophotometer with the KBr pellet technique. The visible and UV absorption spectra were measured using a JASCO V-570 UV/VIS spectrophotometer in the 200–800 nm spectral region. The luminescence spectra were taken on a JASCO FP-6500 spectrofluorimeter equipped with a 150 W xenon lamp as the excitation source at room temperature.

3. Results and discussions

The XRD patterns of SnO_2:Eu sintered at different temperatures between 400 and 1000 °C are shown in Fig. 1. All the reflections are well consistent with JCPDS 41-1445, which confirm the samples as a pure tetragonal rutile crystalline phase of tin oxide and no characteristic peaks of impurities are observed. On the other hand, it is clear to see that the width of the reflections is considerably broadened, indicating that a small crystalline domain size. And the width of the reflections decreases with the increase of heat treatment temperatures, suggesting the enhancement of the particle size. The average crystalline sizes of samples calcined at 400, 600, 800, and 1000 °C, which are determined from (110) crystalline plane, are 7.5, 13.2, 17.6, and 20 nm, respectively. It can be seen that all the particles are in nanometer scale and grow slowly with the increase of heat treatment temperature.

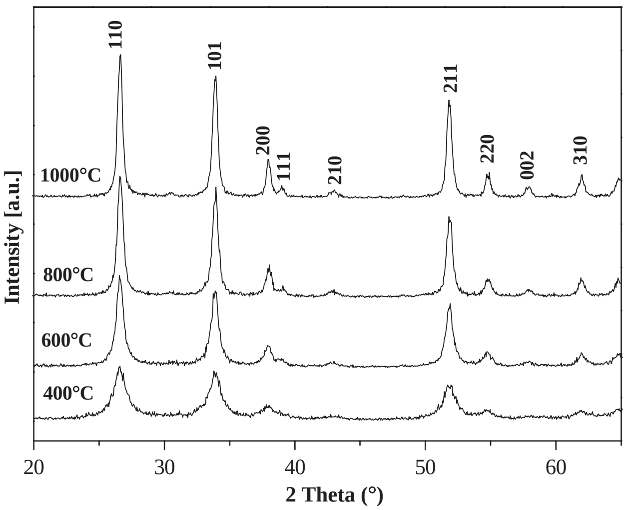

Fig. 1. XRD pattern for SnO_2:Eu particles calcined at four different temperature.

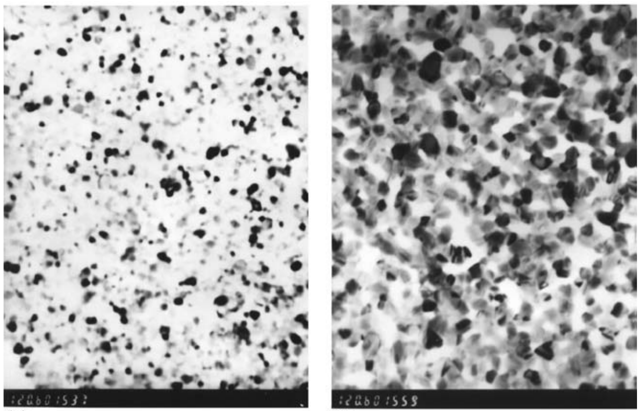
(a) ×120000 (b) ×120000

Fig. 2. Transmission electron micrograph (× 120,000) of SnO_2:Eu samples obtained by different heat treatment at (a) 400 °C (b) 1000 °C.

Fig. 2(a) shows the TEM photograph of the sample heated at 400 °C. The image showed that grains with nearly spherical morphology are homogeneous and well defined. The grain size is nearly 7 nm, which is consistent with the result of XRD. It is well known that higher heat treatment temperature can increase the grain size inevitably. The TEM image of the sample heated at 1000 °C (Fig. 2(b)) verifies that point. But because the carbon network/cages in the polyacrylamide gel can effectively prevent particles agglomeration, even when heated at higher temperatures, the grain size is still below 20 nm.

Fig. 3 shows the FT-IR spectra of the dried gel and the sample after heat treatment at 400 °C for 2 h. As to the sample un-calcined, an intense and very broad IR peak ranging from 3700 to 2500 cm^{-1}, with one maximum at 3180 cm^{-1}, indicate the presence of hydrogen bonds involved in O–H oscillators[12], which may be due to absorbed water and Sn–OH groups. The peaks located at 1664 and 1398 cm^{-1} can be assigned to COO^- group vibration of the citrate complex [13] and the bending vibration of NO_3^- ions occluded in the gel [12], respectively. Two intense broadbands at 617 and 578 cm^{-1} of the pristine sample are associated with the O–Sn–O bridge functional groups and the terminal oxygen vibration of Sn–OH [14]. For the spectrum of sample heated at 400 °C for 2 h (Fig. 3(b)), it is noticed that the only strong peak located at about 616 cm^{-1}, which corresponds to the antisymmetric Sn–O–Sn stretching mode of the surface-bridging oxide formed by condensation of adjacent surface hydroxyl groups [14]. And other absorptions almost disappear. However, we could still observed weaker bands at 1100–1650 and 3000–3500 cm^{-1}, which are probably due to the fact that the spectra are not recorded in situ and the absorption of H_2O, CO_2 from the ambient atmosphere has occurred. These results indicate that the precursors transform to tin oxide completely after calcining at 400 °C for 2 h.

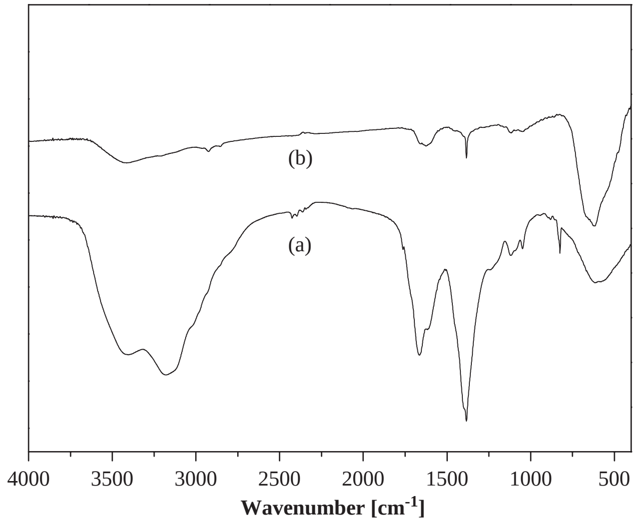

Fig. 3. FTIR spectra for SnO_2:Eu (a) the dried gel and (b) calcined sample at 400 °C.

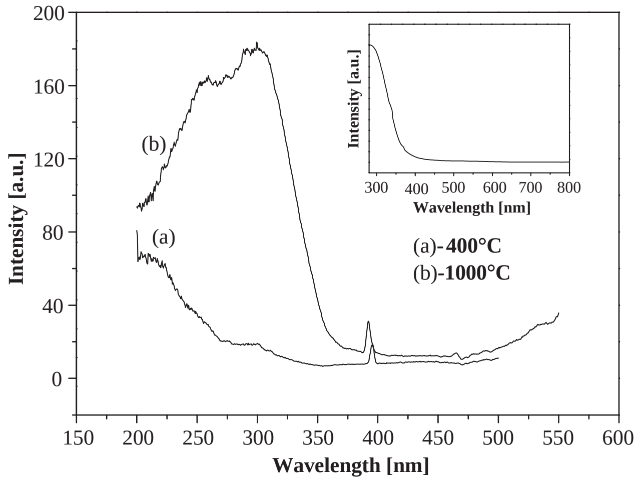

Fig. 4. Excitation spectra ($\lambda_{em} = 590$ nm) for the SnO_2:Eu calcined at different temperature: (a) calcined at 400 °C, (b) calcined at 1000 °C. Inset: diffuse reflect spectrum of nanosized SnO_2 calcined at 1000 °C.

Excitation and absorption spectra of the samples are shown in Fig. 4. The excitation spectrum acquired by fixing the emission wavelength at 590 nm related to Eu^{3+} ion $^5D_0 \rightarrow {}^7F_1$ transition. The inset reveals that the value of the absorption edge of the samples calcined at 1000 °C is 350 nm (about 3.6 eV). The absorption onset of the samples can be assigned to the direct transition of electron in the SnO_2 nanocrystals. In the excitation spectrum, there is a sharp line, located at 395 nm, which can be assigned to the *f–f* transition of Eu^{3+} ions. In addition to this line, there are two broadbands. One band peaking at 260 nm can be assigned to the Eu–O charge transfer. The other band is observed at about 300 nm, which can be assigned to the band-to-band transition of SnO_2 nanocrystal. Its position coincided to the absorption edge energy of SnO_2 crystal, as shown in the insert. The existence of the excitation band corresponding to the band-gap energy is the evidence of the energy transfer from nanosized SnO_2 crystal to the Eu^{3+} ions. The electron–hole pairs are generated by the energy absorbed in the nanocrystals, the energies of which are recombined and then transferred to the Eu^{3+} ions [3]. As seen from the figure, the intensity of the host lattice excitation (300 nm) increased greatly along with higher heat treatment, which indicated that higher heat treatment may enhance the efficiency of energy transfer from SnO_2 crystal to the Eu^{3+} ions remarkably. This will result in the higher PL intensity, just as shown in Fig. 5.

The emission spectra of SnO_2:Eu for the host lattice excitation are shown in Fig. 5. For the samples sintered at 400 and 1000 °C, the spectra both consist of broadband emissions at about 400 and 460 nm, which can be assigned to the luminescence of SnO_2 host. Since the emission maximums are both lower than the band gap of SnO_2 nanocrystal, about 3.6 eV, the visible emission can not be assigned to the direct recombination of a conduction electron in the Sn 5*p* band and a hole in the O 2*p* valence band, but be assigned to the electron

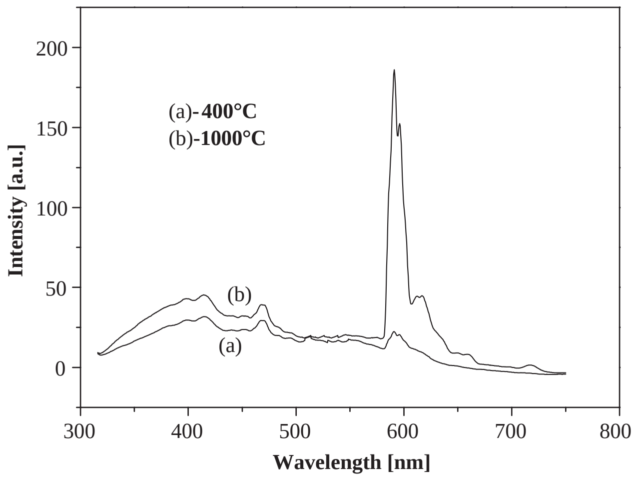

Fig. 5. Emission spectra of SnO_2:Eu samples excited by 300 nm: (a) calcined sample at 400 °C, (b) calcined sample at 1000 °C.

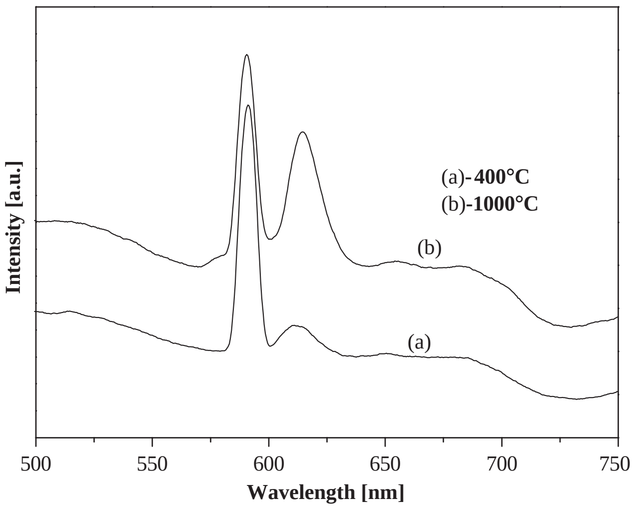

Fig. 6. Emission spectra of SnO_2:Eu samples excited by 395 nm: (a) calcined sample at 400 °C, (b) calcined sample at 1000 °C.

transition, mediated by defects levels in the band gap, such as oxygen vacancies, tin interstitials and so forth [4]. On the other hand, there is a band line located at 590 nm, which corresponds to the magnetic dipole transition of Eu^{3+}. It can be seen from the figure that the intensity of samples sintered at 1000 °C is higher than that sintered at 400 °C, whether for the host emission or for the Eu^{3+} emission. The reasons to the enhanced luminescence intensity may be attributed to more defects produced in SnO_2 via higher heat treatment. Firstly, the incorporation of Eu^{3+} creates the oxygen vacancies because the 1-charge of the Eu_{Sn}^{-} ion has to be compensated for somewhere in the lattice in the form of oxygen vacancy. It is well known that higher heat treatment may accelerate the diffusion of Eu^{3+} ions in SnO_2, which induce more oxygen vacancy formed inevitably. In addition, higher heat treatment (1000 °C) for a long time may destroy the lattice to some extent, which similarly produce more defects. Generally, oxygen vacancies are known to be the most common defects and usually act as radiative centers in luminescence process. That might be the reason why the host emission intensity becomes larger after the samples sintered at 1000 °C. At the same time, the oxygen vacancy might act as the sensitizer for the energy transfer to the RE ion [15]. Since the *f–f* absorption transitions in RE ions are parity forbidden, whereas the SnO_2 is a direct band gap semiconductor, the number of carriers excited through *f–f* transitions in Eu^{3+} ions is much less than that excited through band-gap excitation of SnO_2 [16]. Thus, the enhanced Eu^{3+} emission comes mainly from radiative recombination of the large amount of trapped carriers excited from SnO_2 host. In addition, due to the generation of oxygen vacancies, they will change the symmetry and vibrational modes around the luminescent Eu^{3+} centers, just as seen in Fig. 6.

Fig. 6 shows the emission spectra of the Eu-doped samples calcined at 400 and 1000 °C, respectively, excited at 395 nm (the $^7F_0 \rightarrow {}^5L_6$ transition of Eu^{3+}). There are two emission bands in the spectra. One is the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ at 590 nm and the other is the electrical dipole (ED) transition $^5D_0 \rightarrow {}^7F_2$ at 614 nm. The latter is known for its dependence strongly on the local symmetry of the Eu^{3+} ions. As can be observed from Fig. 6, after calcined at 1000 °C, the intensity of the ED transition $^5D_0 \rightarrow {}^7F_2$ is significantly increased, which means that symmetry of the local environment around Eu^{3+} ions becomes lower after the oxygen vacancies generated.

4. Conclusions

In this paper, we adopted polyacrylamide gel method to prepare nanosized europium doped tine oxide (SnO_2:Eu) successfully. The powders obtained are all below 20 nm with a uniform distribution of the size and shape. The more important is that the as-prepared samples exhibited strong luminescence of Eu^{3+} under the host excitation, which indicated that energy could transfer efficiently from SnO_2 to Eu^{3+} ions.

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