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Improvement of morphology and luminescence of CaS:Eu^{2+} red-emitting phosphor particles via carbon-containing additive strategy

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Abstract CaS:Eu^{2+} red-emitting phosphors particles, were prepared by the precipitation method, followed by sintering in the atmosphere over the mixture of sulfur powder, Na_2CO_3, and carbon-containing compounds such as tartaric acid, citric avid, glucose, and cane sugar. The structure, morphology and photoluminescence performance of the as-prepared samples were investigated by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and photoluminescence spectrum (PL), respectively. The influences of carbon-containing additives on its crystallization behavior, morphology, and enhancement in luminescence of CaS:Eu^{2+} particles were studied. CaS:Eu^{2+} particles without additive show inhomogeneous, rough and aggregation with the size of 75–125 nm, but the spherical particles with mean size of about 110 nm were obtained by adding carbon-containing compounds. Compared with phosphor without additive, the addition of carbon-containing materials induced a remarkable increase of PL, in the order of cane sugar, glucose, citric acid, and tartaric acid. This enhancement is duo to the improvement of crystallinity, particle morphology and size distribution of the samples by adding carbon-containing additive.

Introduction

In recent years, considering the growing importance of energy saving and environmental friendliness, much attention has paid to the phosphor-converted white light-emitting diodes (LED), as solid-state lighting (SSL) devices that consists of a blue or near-UV radiation LED chip and blue/yellow or blue/green/red phosphors [1–3]. The development of SSL, the so-called new generation of lighting devices raised a stringent demand on fluorescent materials. Thus, a hot topic in the field of luminescent materials is to develop novel phosphors or improve existing materials for the conversion of near-UV or blue radiation from LED chips into visible light [4–6]. However, conventional phosphors used in fluorescent lighting are not ideal for SSL, because they have poor absorption on near-UV to blue spectral region. Phosphor which can be effectively excited by blue and near-UV light is lacking, especially the red-emitting one. Red-emitting phosphors are becoming the bottleneck for advancement of white LED innovation [2, 3]. Therefore, it is urgent to seek for suitable and efficient red-emitting phosphors for SSL.

Eu^{2+} is one of the most important and extensively used activators for phosphor materials [2, 3, 7–13]. Eu^{2+}-activated CaS red-emitting phosphors have been widely studied since 1971, because it is an attractive candidates for application in cathode-ray tube display due to its lower brightness saturation for high beam current [7, 8]. Nowadays, the development of SSL has lead to a rebirth of interest in this material because it is strong fluorescent under a wide range of excitation wavelengths, not amenable for photo-bleaching, and of high yield [9, 10]. In addition, CaS host has a high refractive index of 2.1, much closer to the refractive index of LED windows (~2.4), which can increase the escape cone and obtain a better light

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extraction for SSL devices [11]. Eu^{2+}-doped CaS phosphors are usually prepared by reduction of calcium salt containing europium in a toxic H_2S, CO, or CS_2 atmosphere, or by a flux sulfurization method [7–11]. All of these methods require a high sintering temperature and long reaction time which consumed a great deal of the sources of energy in vain, and the products are bulk materials which greatly limits their application in display and lighting devices. More recently, the wet chemical processes which used expensive thioglycerol as capping agent to stabilize the nanoscale CaS, have been adopted to synthesize $CaS:Eu^{2+}$ single crystal [12] or nano-particles for potential application in bioassays [13]. To our best knowledge, there is few report on the synthesis of nano-sized sphere-like $CaS:Eu^{2+}$ particles for SSL. In this work, $CaS:Eu^{2+}$ highly red-emitting phosphor particles were obtained by homogeneous precipitation technique, followed by annealing of the as-obtained precipitate in the presence of mixture of Na_2CO_3, sulfur powder, and carbon-containing additives such as tartaric acid, citric acid, glucose, and cane sugar. The influences of carbon-containing additives on its crystallization, morphology, and luminescence performance were investigated.

Experimental

$CaS:Eu^{2+}_x$ ($x = 0.2$ mol% ~ 4.0 mol%) phosphors were prepared through the precipitation method (PM), by using $Ca(CH_3COO)_2 \cdot H_2O$ (AR) and $Na_2S \cdot 9H_2O$ (AR) as starting materials, $Eu(NO_3)_3 \cdot 5H_2O$ (>99.99%) as dopant. $Ca(CH_3COO)_2 \cdot H_2O$ and $Eu(NO_3)_3 \cdot 5H_2O$ with a cationic molar ratio for Ca:Eu of $(1 - x):x$ ($0.002 \leq x \leq 0.04$) were dissolved in ethanol. A solution of precipitant was prepared by dissolving $Na_2S \cdot 9H_2O$ into ethanol. After 30 min of ultrasonic stirring, the mixed solution of Ca^{2+} and Eu^{3+} was then added dropwise into Na_2S solution under vigorous stirring for 3 h. All precipitates were isolated from the solution by centrifugation and then washed with anhydrous ethanol three times. Finally, the powders were dried in vacuum oven at 80 °C, resulting in precursor powder. For annealing in the atmosphere, the as-obtained precursor powders were placed into a small alumina crucible, which was placed into another crucible of larger diameter. Then both crucibles were put into a crucible of larger volume filled with the mixture of sulfur powder, Na_2CO_3 , and carbon-containing additives such as tartaric acid, citric acid, glucose, and cane sugar, and covered by a lid. The largest crucible with its contents was placed into muffle furnace under N_2 atmosphere and heat-treated at 500–900 °C for 2 h. For comparison, $CaS:Eu^{2+}$ phosphor powder was also synthesized through the above procedure without any additive during annealing.

The powder samples were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and photoluminescence spectrum (PL). The XRD was carried out with a Japan Rigaku D/max-rA rotation anode X-ray diffractometer, using Ni-filtered Cu Kα radiation. TEM images were collected using JEOL JEM-2010 electron microscope. The excitation and emission spectra of powders were recorded using Varain Cary-Eclipse 500 spectrofluorometer equipped with a 60 W Xenon lamp as excitation source. All the measurements were performed at room temperature.

Results and discussion

Europium activated CaS phosphor powders were successfully synthesized by the PM. The body colors of as-obtained powders change from light red, through pink to deep-red as the europium doping concentration increases from 0.2 mol% to 4.0 mol%. Figure 1 shows the XRD patterns of $CaS:Eu^{2+}$ obtained by this method with cane sugar at different firing temperatures and without additive, respectively. With raising annealing temperatures, the peak intensities assigned to main phase CaS increase but the intensities of second phase CaO decrease. When the sintering temperature is above 800 °C (see Fig. 1d, e), the peaks correspond to face-centered cubic structure. Furthermore, as can be seen from Fig. 1e, f the as-obtained $CaS:Eu^{2+}$ phosphor with additive of cane sugar had stronger crystallinity than that without carbon-containing additive at same annealing temperature. This suggest that

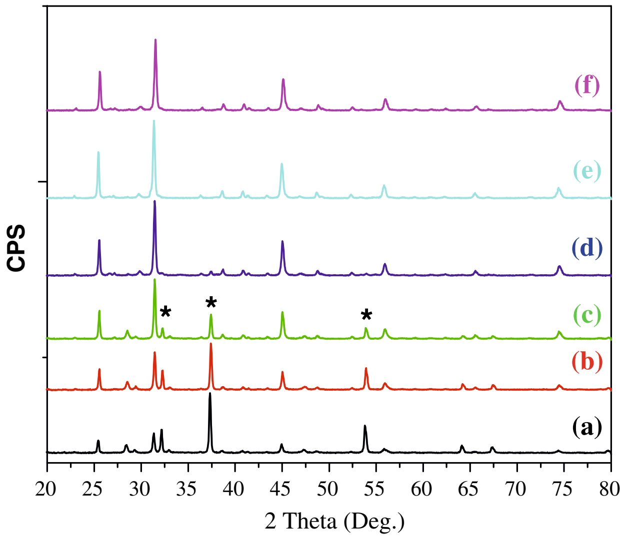

Fig. 1 XRD patterns of $CaS:Eu^{2+}$ obtained by PM with cane sugar under different sintering temperatures: (**a**) 500; (**b**) 600; (**c**) 700; (**d**) 800; (**e**) 900 °C and without additive (900 °C, **f**) (the peaks marked by "*" for CaO phase)

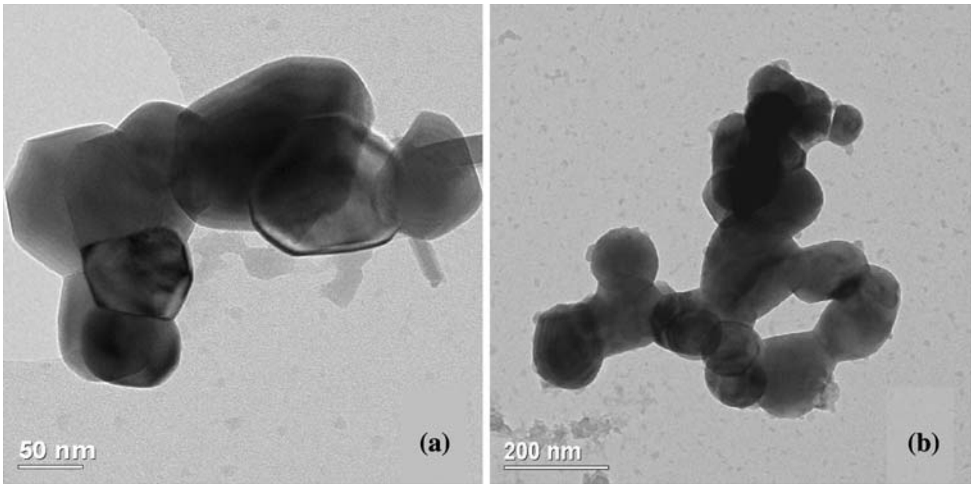

Fig. 2 TEM micrographs of CaS:Eu^{2+} obtained by PM without additive (**a**) and with cane sugar additive (**b**)

the atmosphere over the mixture of Na_2CO_3, sulfur powder, and carbon-containing additives is advantageous to the crystallization of CaS:Eu^{2+} powders.

An ideal phosphor materials must have a non-agglomeration properties, spherical shape and highly crystallinity for good luminescent characteristics. Spherical morphology of phosphors is good for high brightness and high resolution. Additionally, high packing densities and low scattering of light can also be obtained by using spherical phosphors. The aggregation and inhomogeneous shape of phosphors inhibit the absorption of excitation energy and therefore reduce their emission intensity [14, 15]. Luminescent materials with highly crystallinity which have as few lattice defect as possible, can achieve high light output [2]. Thus, the high-temperature sintering is crucial for formation of phosphors, but this procedure always results in serious agglomeration and irregular morphology of the luminescent materials. So, in this study, in aim to obtain spherical particle, carbon-containing additives like tartaric acid, citric acid, glucose, and cane sugar were mixed with sulfur powder and Na_2CO_3 before heat treatment. This mixture was filled into the space between the two crucibles, instead of mixing directly with the precursor powders. Figure 2a shows the TEM micrograph of CaS:Eu^{2+} prepared by the PM without additive. The particles were inhomogeneous, rough and agglomeration with size of 75–125 nm. The typical TEM micrograph of CaS:Eu^{2+} obtained by the PM with cane sugar additive is presented in Fig. 2b. It exhibits smooth, uniform and nearly spherical-like morphology with a mean particle size of about 110 nm, which can be effective for forming a good phosphors layer with higher packing density and lower surface scattering suitable for manufacture of white LED. The surface of the particles became smooth after adding carbon-containing additive during high-temperature annealing. This result demonstrates an obvious advantage of heat-treating of

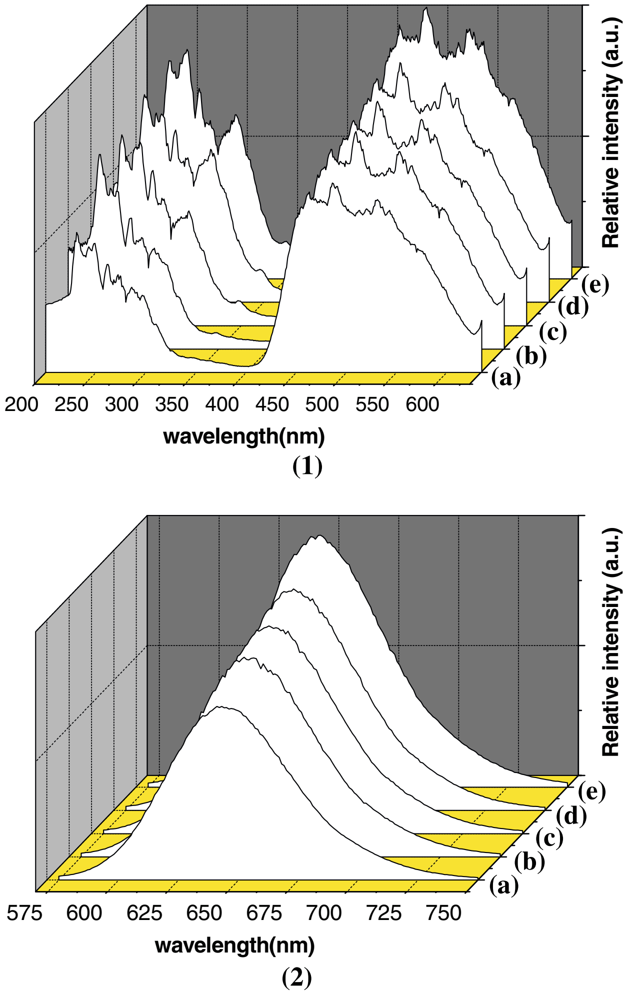

Fig. 3 Excitation (**1**, Monitoring wavelength: $\lambda_{em} = 645$ nm) and emission (**2**, Excitation wavelength: $\lambda_{ex} = 470$ nm) spectra of CaS:Eu^{2+} by PM without additive (**a**) and with different additives: (**b**) tartaric acid; (**c**) citric avid; (**d**) glucose; (**e**) cane sugar

the precipitate in the atmosphere over the mixture of sulfur powder, Na_2CO_3, and carbon-containing additives, and the separation of sample and the multi-component mixture in the space.

Excitation and emission spectra of CaS:Eu^{2+} with different additives and without additive are depicted in Fig. 3-1, 2, respectively. The excitation spectrum of CaS:Eu^{2+} phosphor consists of two broad bands: the one is in the rang 200–365 nm with the peak position at 252 nm, the second one located at the range of 400–625 nm. Both of these excitation bands are attributed to $4f^7(^8S_{7/2}) \rightarrow 4f^65d(t_{2g})$ transition of Eu^{2+} ions [3]. The most distinguishing feature of excitation spectrum of CaS:Eu^{2+} phosphor is the strong absorption to blue radiation, which makes it a good candidate for LED application. Under excitation of 470 nm blue light (see Fig. 3-2), all phosphors exhibit red emission peaked at 645 nm which is due to the $e_g \rightarrow t_{2g}$ transition of Eu^{2+} ions [3]. As shown in Fig. 3-1, 2, the addition of carbon-containing additive can enhance excitation and luminescence intensity in the order of cane sugar, glucose, citric acid, and tartaric acid, compared with the phosphor without additive. In other words, among four additives used in this work, the cane sugar is better than the others. The reason why the cane sugar is superior to the others additives might be contributed to its biggest number of carbon atom in cane sugar among four additives. This enhancement fits well with the above results of XRD and TEM.

In order to find a best doping concentration of europium ions in this phosphor, a series of samples with various Eu^{3+} concentrations were prepared. Integrated emission intensity of 645 nm under 470 nm excitation was calculated. Figure 4 shows the dependence of 645 nm emission intensity of CaS:Eu^{2+} on dopant content of Eu^{3+} ions. It is found that emission intensity firstly increases up to 1.0 mol%, and then decreases when activator concentrations continuously increase. The emission intensity reaches the maximum at 1.0 mol% doping europium ion. In other words, concentration quenching occurs when Eu^{3+} doping concentration is beyond $x = 1.0$ mol%. This concentration quenching effect might be due to the strong dipole-dipole interaction of Eu^{2+} ions [3, 16]. So the optimum concentration of europium ions in CaS:Eu was about 1.0 mol% of Ca^{2+}, which is higher than that by other wet chemical processes (0.85 mol%) [13]. Higher quenching concentration was beneficial for further enhancing the luminescent intensity.

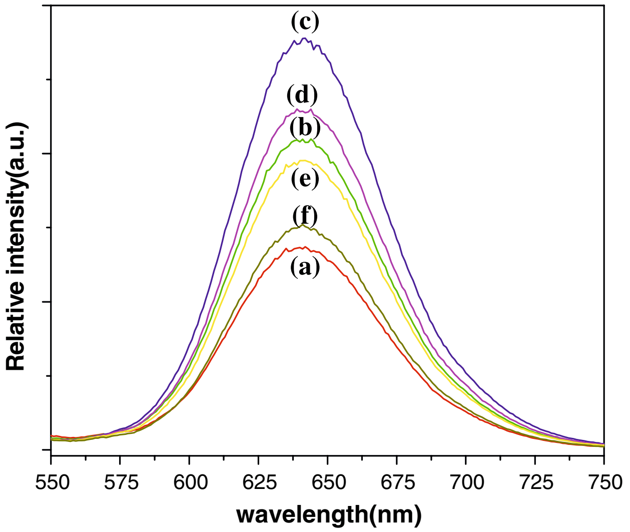

Fig. 4 The dependence of 645 nm emission intensity of CaS:Eu^{2+} with cane sugar additive on dopant content of europium ions: (**a**) 0.2, (**b**) 0.5, (**c**) 1.0, (**d**) 2.0, (**e**) 3.0, (**f**) 4.0 mol% ($\lambda_{ex} = 470$ nm)

Conclusion

CaS:Eu^{2+} phosphor particles with spherical morphology, fine size and non-aggregation characterization, were successfully prepared via a precipitation method under the existence of carbon-containing compound. The effect of carbon-containing additives on its crystallization, morphology and luminescence of CaS:Eu^{2+} particles was investigated. Compared with that of phosphor without additive, excitation and emission intensity of samples with addition of carbon-containing compounds are obviously enhanced, in the order of cane sugar, glucose, citric acid, and tartaric acid. This improvement of luminescence was analyzed in details. The relationship between luminescent intensity and doping concentration of europium ions was also investigated. The samples exhibited a higher quenching concentration of europium ions in comparison with those prepared by other wet chemical processes. The strong excitation broad band of the as-obtained CaS:Eu^{2+} phosphor matches maximum output wavelength of blue LED chips, and emits red luminescence peaked at about 645 nm. Therefore, this material is promising for applications in solid-state light devices based on blue LED chips.

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