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Preparation of CaS: Ce, Sm films by sol-gel method

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CaS: Ce, Sm films were fabricated by a sol-gel method, subsequently annealed at 500 °C for 1 hr in N₂ atmosphere. The optimum mole ratio of $C_2H_4(OH)_2$ to Ca^{2+} is 2 : 1. The XRD results show that CaS: Ce, Sm is face-centered cubic structure and the lattice constant increases 0.07 Å along all directions. Its diffraction peak has a certain broadening and moves to small angel, which is due to the surface effect of the nano particles. The AFM results show that the average grain size of CaS: Ce, Sm films is 30 nm and the grain size distribution is uniform. The strong emission peaking at 626 nm with 420 nm as excitation light corresponds to the ${}^{6}H_{5/2} \rightarrow {}^{4}M_{19/2}({}^{6}P, {}^{4}P)_{5/2}$ transition.

Key words: CaS: Ce, Sm, Sol-gel method, Luminescent spectrum.

Introduction

Alkaline earth sulphide has been known as excellent luminescent material for a long time. There are many literatures on this luminescent material, which include Lehmann's pioneering works. Recently, more attention was attracted because of the potential uses in many fields, for example, optical storage, radiation dosimetry, optical computing [1, 2], cathode ray tubes, infrared sensors, thermoluminescence and electroluminescence panels [3]. CaS doped with double rare earth ions is a kind of luminescent materials with the infrared excitation. The dopants may act as trapping, recombination, luminescence centers in the host, and also play an important role in energy storage. Traditionally, this luminescent material is synthesized by solid-state reaction [4, 5], but which usually needs mechanical mixing and high temperature sintering for a long time, and introduces additional impurities and defects to the final material. Recently, some new methods have been found for synthesis of this luminescent material, such as sol-gel processing, hydroxide co-precipitation, homogeneous precipitation, glycothermal treatment and combustion synthesis. CaS: Ce, Sm films offer significant advantages over conventional bulk powders, such as higher resolution, more uniform density and higher thermal stability [6]. More and more attention has been paid to CaS: Ce, Sm films due to its potential applications in electroluminescent displays, plasma display panels, field emission displays and mercury-free lamps. CaS: Ce, Sm films can be fabricated by a variety of methods, such as chemical vapor deposition, spray pyrolysis, pulsed laser deposition and sol-gel processing [8]. Previously, some research

has shown that CaS: Ce, Sm films synthesized by chemical vapor deposition exhibit lower luminous efficiency than powder. Because this method is difficult to control stoichiometric ratio and crystallinity of the host lattice is poor [7, 9]. Moreover, high quality CaS: Ce, Sm films are synthesized difficultly by chemical vapor deposition because of the high vaporization temperature, the high activation temperature and the instability of alkaline earth sulphides in air.

Compared with the other methods, the sol-gel method has been confirmed to have more advantages in lower firing temperature, distributing the activator ions homogeneously [10, 11] and improving the emission efficiency for CaS: Ce, Sm. In addition, sol-gel technology is suitable for deposition of CaS: Ce, Sm films, which have extensive applications in many fields [12].

Until now, CaS: Ce, Sm films fabricated by a sol-gel method has not been reported. In this paper, CaS: Ce, Sm films were prepared by sol-gel method. The microstructure, morphology and luminescent properties of CaS: Ce, Sm films were investigated by XRD, AFM, excitation and emission spectra.

Experimental procedure

Ca(AC)₂, CH₄N₂S, ethylene glycol, Ce(NO)₃·6H₂O, Sm₂O₃ were used as starting materials. Firstly, Ca(AC)₂ and CH₄N₂S in a mole ratio of 1 : 1 were mixed and dissolved in ethylene glycol and distilled water (solution A). Sm₂O₃ was dissolved in HNO₃ and added into solution A with Ce(NO)₃ · 6H₂O under magnetic stirring at room temperature according to each concentration of Sm and Ce which was controlled at 0.1 mol%. HNO₃ was added dropwise into this solution and stirred for 2 hrs in water bath with 40 °C to form sols, and the pH value of the solution was kept between 3 and 4. Then, the thoroughly cleaned quartz glass substrates were

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dipped into the sols vertically and withdrawn at a speed of 2 cm/s. The as-prepared transparent films were dried at room temperature in air. The above-mentioned coating processes were repeated three times to increase the film thickness. Finally, the substrates were heat-treated at 500 °C for 1 hr in nitrogen atmosphere.

The X-ray diffraction (XRD, Rigaku-D/max 2200PC) of the powders and films were examined. The morphology of the crystalline film samples was inspected using an atomic force microscope (AFM, SPI3800N) with tapping mode. The excitation and emission spectra were taken on a Hitachi F-4600 spectrofluorimeter equipped with a 150 W xenon lamp as the excitation source. All the measurements were performed at room temperature.

Results and discussion

When hydrolysis reached a certain degree in the preparation process of sol, particle agglomerate appeared to form precipitate, which was bad for precursor sol. The reaction process is as follows:

 $Ca(AC)_2+H_2O \Leftrightarrow HO-CaCOCH_3+HOCOCH_3$ (1)

$$HO-CaCOCH_3+H_2O \Leftrightarrow Ca(OH)_2+HOCOCH_3$$
 (2)

The complexation reaction of ethylene glycol with Ca^{2+} decreases the Ca^{2+} hydrolysis activity to form a homogeneous and stable precursor. The experiment results in different mole ratio of $Ca(AC)_2$ and $C_2H_4(OH)_2$ show that the precipitates don't appear during heating and stirring sol when n $C_2H_4(OH)_2$: n $Ca^{2+} \ge 2$. Because com-plexation between ethylene glycol and Ca^{2+} stops hydrolysis of calcium acetate, homogeneous and steady precursor was formed. But excess ethylene glycol make the gel time extended, which is bad for the preparation of the films. So the optimum mole ratio of $C_2H_4(OH)_2$ to Ca^{2+} is 2 : 1.

The XRD patterns of CaS: Ce, Sm films prepared by sol-gel method with annealed at 500 $^{\circ}$ C for 1 h in N₂



Fig. 1. XRD patterns of CaS: Ce, Sm films and host CaS prepared by sol-gel method and annealed at 500 $^{\circ}$ C for 1 hr in N₂ and air atmospheres.

and air atmospheres are shown in Fig. 1. As shown in Fig. 1, the main phase of the sample annealed at 500 °C for 1 hr in air atmosphere is CaSO₄. Because CaS is oxidised easily into CaSO₄ in air atmospheres. The complexation reaction of ethylene glycol with Ca²⁺ decreases the Ca2+ hydrolysis activity. CH4N2S is dissolved in water to form Ca-S coordination. The sintering process includes two parts, as shown in the following equations 3-4. But whole reactants annealed at 500 °C for 1 hr in air atmospheres didn't react completely. A small amount of carbon cannot be oxidized into gas to move out of the sample, and exist in the form of black powder CaCO₃. The existence of carbon cannot be investigated by XRD because of which existing in the form of amorphous carbon. Therefore, the characteristic peaks of reactant Ca2SiO4, intermediate CaCO3 and endproduct CaSO₄ can be observed in Fig. 1.

 $Ca(OCOCH_3)_2 + C(NH_2)_2S + \frac{11}{2}O_2 \rightarrow CaS + N_2 + 5CO_2 + 5H_2O$ (3)

$$CaS+2O_2 \rightarrow CasO_4 \tag{4}$$

The CaS oxidation is inhibited by strictly controlling the oxygen partial pressure. As shown in Fig. 1, the codoped sample annealed at 500 °C for 1 hr in N₂ atmosphere is single phase CaS, and there is no obvious characteristic peaks of Ce and Sm in XRD patterns. The XRD patterns for CaS: Ce, Sm have no significant difference with CaS. Because the addition amount of Ce and Sm are few (0.1 %mol) and don't react with host CaS to form a new substance. The results of XRD indicate CaS: Ce, Sm films annealed at 500 °C for 1 hr in N₂ atmosphere exhibit face-centered cube structure, the average grain size is about 30 nm. The diffraction peaks were broadened due to small size effect of the nanometer grain. Table 1 shows the variation in 2θ for the most intense (200) peak, interplanar spacing d and lattice constant of CaS and CaS: Ce, Sm. It is found that there is slight variation in the lattice constant with the addition of cerium and samarium. The lattice constant of CaS: Ce, Sm films increases 0.07 Å along all directions and its diffraction peak moves to small angel, which can mainly be attributed to large specific surface, high surface activity and surface tension characteristics. As the offset is too small, it is difficult to show the left offset of the XRD patterns by comparison between CaS: Ce, Sm and CaS in Fig. 1. But for the most intense (200) peak, Table 1 shows that value of 20 of CaS: Ce, Sm is less than

Table 1. Value of 2θ for the most intense (200) peak, interplanar spacing d and lattice parameter for CaS and CaS: Ce, Sm.

Sample specifica- tion	20 (deg.)	d (Å)	Lattice parameter (Å)
CaS	31.416	2.8451	5.6903
CaS: Ce, Sm	31.020	2.8806	5.7611



Fig. 2. AFM image of CaS: Ce, Sm films prepared by sol-gel method and annealed at 500 $^\circ$ C for 1 hr in N₂ atmosphere.



Fig. 3. Spectra of (a) excitation ($\lambda_{ex} = 420 \text{ nm}$) and (b) emission ($\lambda_{em} = 626 \text{ nm}$) of CaS: Ce, Sm films prepared by a sol-gel method and annealed at 500 °C for 1 hr in N₂ atmosphere.

CaS, which demonstrates that there is the left offset with the increase of the lattice constant in the XRD patterns of CaS: Ce, Sm.

The AFM image of CaS: Ce, Sm films prepared by a sol-gel method and annealed at 500 °C for 1 hr in N_2 atmosphere is shown in Fig. 2. It is found that the surface of CaS: Ce, Sm films is relatively flat, and the sample has homogenous grains with average size about 30 nm and clear boundary, which is almost consistent with the results of XRD.

Excitation and emission spectra of CaS: Ce, Sm films (500 $^{\circ}$ C, 1 hr, N₂ atmospheres) are presented in Figs. 3(a) and 3(b). The characteristic linear excitations originating from the ground state ${}^{6}H_{5/2}$ of Sm³⁺ to different excited states ${}^{4}K_{17/2} + {}^{4}L_{17/2} (\sim 345 \text{ nm}), {}^{4}L_{17/2} (\sim 375 \text{ nm}), {}^{4}K_{11/2} (\sim 375 \text{ nm}), {}^{4$ $_{2}(\sim 404 \text{ nm}), \quad {}^{4}M_{19/2} + {}^{6}P_{5/2} + {}^{4}P_{5/2}(\sim 420 \text{ nm}), \quad {}^{4}I_{13/2} + {}^{4}I_{9/2}$ $_{2}(\sim 470 \text{ nm})$ are detected in the excitation spectrum. According to the PL excitation spectrum intensity, 345 nm, 375 nm, 404 nm, 420 nm and 470 nm can be chosen as excitation light. But the excitation peaks at 345 nm, 375 nm, 404 nm and 470 nm are very weak. The strong emission is at 626 nm with 420 nm as excitation light, which is accord with references about the luminescence spectra of Sm³⁺. The emission peaks at 505 nm and 565 nm at an excitation wavelength of 450 nm for CaS: Ce, Sm may be confirmed as the characteristic emission of Ce in CaS host [13]. But, Fig.

Conclusions

CaS: Ce, Sm films were fabricated by sol-gel method at 500 °C for 1 hr in N₂ atmosphere. The optimum mole ratio of C₂H₄(OH)₂ to Ca²⁺ is 2 : 1. CaS: Ce, Sm is facecentered cubic structure, and the lattice constant increases 0.07 Å along all directions. Its diffraction peak compared with the host CaS has a certain broadening and moves to small angel, which is due to the surface effect of the nano particles. The strong emission peaking at 626 nm with 420 nm as excitation light corresponds to the ${}^{6}H_{5/2} \rightarrow {}^{4}M_{19/2} + {}^{6}P_{5/2} + {}^{4}P_{5/2}$ transition. CaS: Ce, Sm is a new material suitable for sun-light conversion film.

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