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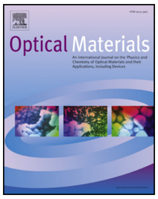

Photophysical properties of Eu^{3+}-doped $C_{12}H_{14}O_{16}Zn_3$ phosphor obtained by a facile hydrothermal method

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ABSTRACT

Zinc citrate is an organic salt complex prepared with organic carboxylate and inorganic cation. In the study, a series of C12H14O16Zn3: Eu3+ phosphors were synthesized through a facile hydrothermal method and then the as-prepared phosphors were characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM), and photoluminescence (PL) spectrometer. The morphology of $C_{12}H_{14}O_{16}Zn_3$: Eu^{3+} phosphors was a flake with the size of 1 ~ 10 μm × 0.5 ~ 5 μm and the length-width ratio of 0.2–20. The strongest emission peak of $C_{12}H_{14}O_{16}Zn_3$: Eu^{3+} at 621 nm was ascribed to $^5D_o \rightarrow {}^7F_2$ transition of Eu^{3+} and the peaks centered at 590, 653 and 702 nm respectively corresponded to $^5D_o \rightarrow {}^7F_1$, $^7F_3$, and $^7F_4$ transitions. $C_{12}H_{14}O_{16}Zn_3$: Eu^{3+} gave the red light emission, as indicated by color coordinate analysis. The photoluminescence intensity of the phosphors prepared under the Eu^{3+} concentration of 7% was the highest. As a new kind of phosphor, $C_{12}H_{14}O_{16}Zn_3$: xEu particles may be applied in biological fluorescent tags and luminescent materials.

1. Introduction

Rare earth organic complexes as new fluorescent materials have been extensively explored due to their wide application potential in many fields such as fluorescent probes [1], light-emitting diodes [2], acidic catalysts [3], biological sensors [4], and medical magnetic resonance imaging [5]. Reported rare earth organic complexes include 6-*p*-Chloroaniline carbonyl 2-pyridine carboxylic acid europium complex [6], the complexes of Eu(III) and Gd(III) with pyrazine-2-carboxylic acid [7], and aromatic carboxyl acid-functionalized polysulfone Eu(III) and Tb(III) complexes [8]. However, lanthanide complexes had some disadvantages, such as high cost, complex synthesis steps, low synthesis yields, low product purity, and poor thermal stability, which limited the application scope of lanthanide complexes [9,10].

As a strong organic acid, citric acid can be easily chelated with metal ions to form citrate [11,12]. In 2005, Shenggui Liu [13] synthesized C6H7EuO8 and C6H7TbO8 by respectively mixing citric acid with Eu2O3 and Tb4O7 and found that the two polymeric complexes had good luminescent properties. Lanthanide ions were not only an important component but also a luminescence center. Numerous rare earth oxides were tested in the synthesis of $C_6H_7EuO_8$ and $C_6H_7TbO_8$. On the basis of the $C_6H_7EuO_8$ and $C_6H_7TbO_8$ complexes, we believed that it was possible to incorporate lanthanides into host matrices with the better stability to overcome the shortcomings of rare earth organic complexes. According to the idea, we chelated alkali metal ions with citric acid and successfully obtained europium ion-doped $C_{12}H_{18}Ca_3O_{18}$ phosphors, which gave red-light emission [14]. We found that alkali metal matrix was not better than transition metal matrix in the synthesis of excellent properties phosphors because transition metals could sensitize the near-infrared luminescence of rare earth ions and were widely accessible and cheap [15]. Therefore, we believed that it was feasible to synthesize matrices by chelating transition metals with citric acid. Zinc is a kind of transition metal and can be easily chelated with citric acid to form zinc citrate. In the structure of zinc citrate, the central zinc atom is bonded to hydroxyl groups and intermediate carboxyl groups of two citric acids as well as one terminal carboxyl group of each citric acid to form an octahedral structure of zinc. Zinc citrate has a simple structure and owns high structural stability and thermal stability, so it may be a promising organic carboxylate matrix material [16].

Zinc citrate is an organic salt complex prepared with organic carboxylate and inorganic cation. In this paper, in order to introduce Eu3+ into the preparation process of zinc citrate, a tiny part of zinc citrate was converted into europium citrate to form a new luminous powder. As a luminescence center, rare earth ions were greatly reduced. The preparation process had several significant advantages, such as the

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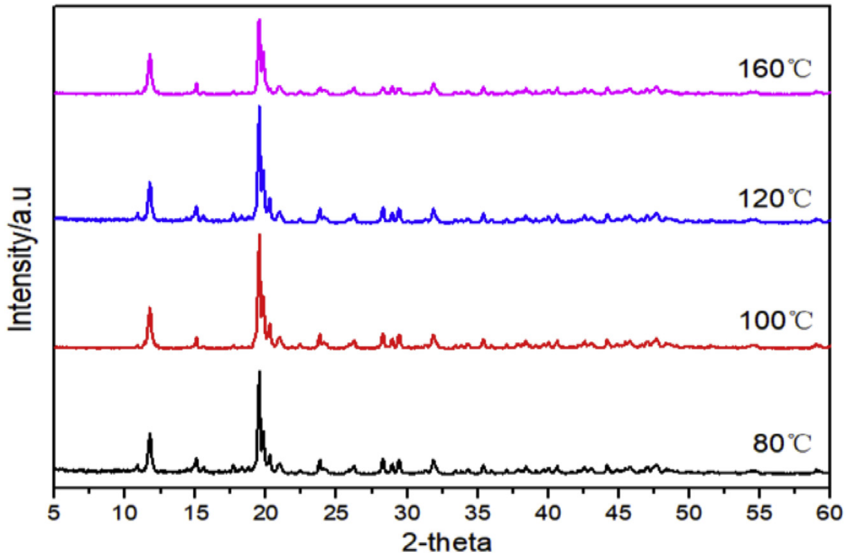

Fig. 1. XRD patterns of the C12H14O16Zn3: x Eu3+ (x = 5%) samples obtained at different hydrothermal temperatures from 80 to 160 °C.

simple preparation technology, mild reaction conditions, and low cost. Eu-doped zinc citrate phosphor may be applied in biological fluorescent tags and luminescent materials.

2. Experimental

2.1. Materials

The precursor materials included Zinc nitrate ($Zn(NO_3)_2.6H_2O$, 96.0%), trisodium citrate ($C_6H_5Na_3O_7{\cdot}2H_2O$, 99.0%), concentrated nitric acid (HNO_3, AR) and anhydrous ethanol (C_2H_6O, 99.7%) purchased from Chengdu Kelong Chemical Co., Ltd., Chengdu, China. Europium oxide (Eu_2O_3, 99.9%) was bought from Haiyingyuan Chemical Co., Ltd. Distilled water was used in the experiment and all the chemicals were directly used without further purification.

2.2. Methods

$C_{12}H_{14}O_{16}Zn_3$: Eu^{3+} phosphors were prepared according to the hydrothermal method with the stoichiometric amounts of Zn(NO3) 2.6H2O and C6H5Na3O$_7$·2H$_2$O. Solution I was prepared by dissolving a certain amount of zinc nitrate in distilled water at room temperature. Solution II was prepared by dissolving a certain amount of sodium citrate in distilled water at room temperature. The $Eu(NO_3)_3$ solution was prepared by dissolving stoichiometric amounts of Eu_2O_3 in HNO_3 at an elevated temperature and used as Solution III.

Solution I and Solution III were mixed together under constant stirring for 10 min at room temperature. After that, Solution II was added into the above mixture solution under constant stirring for 5 min at 60 °C. Then anhydrous ethanol was added into the mixture to precipitate zinc citrate. Then, the as-obtained mixture was centrifuged and washed with water and ethanol for several times to remove sodium nitrate. In addition, PH was controlled within the acidic range throughout the entire reaction process. Subsequently, the obtained milky colloidal solution was transferred to a 100.0-mL stainless-steel reactor with Teflon liner for the immediate hydrothermal reaction at 180 °C for 24 h. After naturally cooling to room temperature, the final reaction products were obtained by centrifugation and freeze-drying. The reaction is as follows:

$3Zn\ (NO_3)_2.6H_2O + 2Na_3C_6H_5O_7{\cdot}2H_2O \rightarrow C_{12}H_{14}O_{16}Zn_3 + 6NaNO_3 + 2H_2O$. (1)

2.3. Characterization

The crystal structures of final products were analyzed by DX-2700 X-ray diffractometer (Dandong Fangyuan Instrument Co., Ltd.) with Cu-Ka radiation (40 kV, 40 mA). The microstructures and morphologies of the samples were examined with Carl Zeiss Evo18 scanning electron microscope (SEM).

The luminescence spectra were measured with Hitachi FL-4600 fluorescence spectrometer.

The decay curves were measured with Hitachi FL-4600 fluorescence spectrometer. The monitoring wavelength was set at 621 nm under the excitation at 393 nm. The decay curves were fitted in the software Origin. The fitted result showed that A1 ≠ A2 and t1 ≠ t2. Therefore, the decay curves of all phosphors are well fitted by the second-order exponential function as follows:

$$y = y_0 + A_1\, exp\frac{X_0 - X}{\tau_1} + A_2\, exp\frac{X_0 - X}{\tau_2} \tag{2}$$

where τ_1 and τ_2 represent the luminescence decay time. The value of decay time can be calculated as [17]:

$$\tau = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \tag{3}$$

All the measurements were performed at room temperature.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows XRD patterns of $C_{12}H_{14}O_{16}Zn_3$: Eu^{3+} (x = 5%) phosphors synthesized at different hydrothermal temperatures from 80 to 160 °C. All samples had some obvious peaks and similar diffraction spectra. When the reaction temperature was 80 °C, the diffraction pattern had the characteristics of narrow half peak width and relatively high diffraction peaks, suggesting that its crystallinity was not bad. As the hydrothermal temperature increased to 100 °C, the intensities of diffraction peaks of the obtained samples became higher, indicating the enhancement of crystalline. When the reaction temperature was increased to 120 °C, the crystallinity of the obtained samples was optimized and diffraction peak intensity increased slightly. When the temperature was further increased to 160 °C, the crystallinity of the obtained samples showed no obvious difference compared with that of the samples obtained at 120 °C. The XRD patterns of the samples treated