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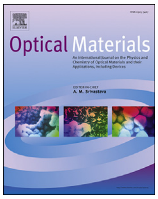

Synthesis and photoluminescence of Eu^{3+} doped $CaGd_2(WO_4)_4$ novel red phosphors for white LEDs applications

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ABSTRACT

To provide a systematic study of scheelite structure tungstates, potentially better red phosphors, series of $CaGd_{2-x}(WO_4)_4$:Eu_x were successfully synthesized by the conventional solid state method. X-ray powder diffraction, scanning electron microscopy, fluorescence spectra, decay lifetime measurement and Judd-Ofelt theory were used to investigate the properties of $CaGd_2(WO_4)_4$:Eu^{3+} phosphors. The results reveal that $CaGd_2(WO_4)_4$ compound has monoclinic system with space group *I*2/*b*. Under the excitation at 393 nm, Eu^{3+} doped $CaGd_2(WO_4)_4$ phosphor exhibits the dominant red emission peak located at 616 nm, which is ascribed to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ion. Effect of the calcination temperature on the photoluminescence properties has also been studied and it is found that the emission intensity reaches the maximum at 1273 K. In addition, the optimal doping concentration of Eu^{3+} is determined to be $x = 0.8$. It can be confirmed that the dipole-dipole interaction type plays an important role in the energy transfer in $CaGd_2(WO_4)_4$:Eu^{3+} phosphors through the concentration quenching curve. The Judd-Ofelt parameters Ω_2 and Ω_4 have been calculated, indicating the lower site symmetry and higher covalency around Eu^{3+} ions. The CIE coordinates of $CaGd_{1.2}(WO_4)_4$:$0.8Eu^{3+}$ phosphors are $x = 0.649$ and $y = 0.349$, which are close to the standard of NTSC. These results show that $CaGd_2(WO_4)_4$:Eu^{3+} phosphor can be a potentially better red emitting phosphor for white light emitting diodes (LEDs).

1. Introduction

White light-emitting diodes (LEDs), as a new-type of solid state light source, are known as green-light source due to their advantages of energy conservation, environmental friendliness, long lifetime and high reliability [1,2]. The most commercially available white LEDs are a combination of a blue-emitting LED chip with yellow phosphors ($Y_3Al_5O_{12}$:Ce^{3+}). However, this type of white LED has poor color rendering index (CRI) because of the color deficiency in the red region [3]. One approach to solve this problem is to combine blue/green/red tricolor phosphor layers on the output surface of a near-UV (~400 nm) InGaN-based LED. The performance of these w-LEDs strongly depends on the luminescent properties of the adopted phosphors. Presently, the commercially available tricolor phosphors are the red emitting (Y_2O_2S:Eu^{3+}), green emitting (ZnS:Cu^+,Al^{3+}) and blue emitting ($BaMgAl_{10}O_{17}$:Eu^{2+}). Nevertheless, in comparison with blue and green phosphors, the current red-emitting phosphor shows lower fluorescent efficiency and poor stability [4,5]. Therefore, in order to improve the performance of the w-LEDs, it is necessary to develop better and efficient red emitting phosphors that can be excited effectively by near UV.

In the meantime, rare earth Eu^{3+} ion doped luminescent materials have gained much attention, because of their interesting optical properties originating from Eu^{3+} ion partially filled 4f-shell. Various Eu^{3+} ion doped phosphors have been investigated extensively, such as Eu^{3+} ion doped silicate phosphors [6,7], vanadate phosphors [8,9], phosphate phosphors [10,11], tungstate and molybdate phosphors [12–14]. Among them, the scheelite -type tungstate host with formula $(A',A'')_m[(B',B'')O_4]_n$, where A',A'' = alkali elements, alkaline -earth elements, rare earth elements; B',B'' = Mo,W, have been extensively studied as high efficiency red phosphors, due to their broad and strong charge transfer band (CTB), which provides efficient energy transfer from the tungstate host to the activators (Eu^{3+}), and in turn generates intense red emission. For example, Maheshwary et al. [15] synthesized $SrWO_4$:Eu^{3+} nanophosphors with various Eu^{3+}

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concentrations by a polyol synthesis route, and investigated the effect of annealing temperature and doping concentration on the photoluminescence properties of phosphors. The results revealed that an intense red emission was observed with a strong peak at 613 nm due to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ion. Li et al. [16] prepared two system Eu^{3+} doped double tungstates phosphors $MLa(WO_4)_2$ (M = Li, Na, K) and $NaRE(WO_4)_2$ (RE = Gd,Y, Lu) by solid state reaction, and studied the optical properties of these phosphors in detail. Rasu K et al. [17] manufactured Eu^{3+}:$KLa(WO_4)_2$ novel red phosphors through Pechini type sol-gel method, and discussed the radiative properties of the compound by calculating Judd-Ofelt parameters from the emission spectra. All these studies suggest that Eu^{3+} doped the scheelite-type tungstates may be potential red-emitting phosphors for white LEDs due to their excellent luminescence properties.

As a novel member of the scheelite structure tungstates, $CaGd_2(WO_4)_4$ phosphor belongs to the monoclinically distorted scheelite structure, associated with the space group of $I2/b$, and lattice parameters of a = 5.2202 Å, b = 5.2388 Å, c = 11.4085 Å,γ = 90.994°, V = 311.95 and Z = 1 [18]. In this compound, the Ca^{2+}/Gd^{3+} ion forms distorted polyhedron [Ca/GdO_8] with its surrounding eight oxygen ions, and W^{6+} ion creates tetrahedron [WO_4] with its surrounding four oxygen ions. The tetrahedrons [WO_4] are coordinated by four [Ca/GdO_8] square antiprisms through common O ions and form a 3D framework. In comparison to $CaWO_4$ with the tetragonal symmetry (space group $I4_1/a$), the substitution of Ca^{2+} in $CaWO_4$ by Ca^{2+} and Gd^{3+} leads to the formation of $CaGd_2(WO_4)_4$. However, there are 25% of cation vacancies in the structure due to the $(Ca^{2+}+Gd^{3+})$:(WO_4) ratio different from 1:1, which results in changing the structure from tetragonal symmetry to monoclinic symmetry, and the 3D point symmetry from C_{4h} to C_{2h}. As a result, the Eu^{3+} ion occupies a site with at most C_2 site symmetry when Eu^{3+} ion replace Gd^{3+} ion. According to Judd-Ofelt theory, the lack of inversion symmetry induces the higher luminescence intensity of the hypersensitive $^5D_0$–$^7F_2$ transition and better color purity [19,20]. Furthermore, in the $CaGd_2(WO_4)_4$ structure, the distance between Eu^{3+} ions is longer, because of the larger O–W–O and Eu–W–O bond angles, which leads to a high quenching concentration of Eu^{3+}. Although the structure characteristic of $CaGd_2(WO_4)_4$:Eu^{3+} seems to suggest that, it might be a more efficient red emitting phosphor for the w-LED application, up till now, few systematic studies are found, to cover the synthesis and luminescence properties of $CaGd_2(WO_4)_4$:Eu^{3+} phosphors under the near-UV excitation.

Hence, in this work, we provide a systematic study of Eu^{3+} doped $CaGd_2(WO_4)_4$ red phosphors. $CaGd_2(WO_4)_4$: Eu^{3+} phosphors were synthesized successfully by the conventional solid-state method, and their structure, morphological and photoluminescence properties of $CaGd_2(WO_4)_4$:Eu^{3+} phosphors were investigated in detail. The results show that $CaGd_2(WO_4)_4$:Eu^{3+} phosphors have indeed better red color purity and higher quenching concentration, due to the lower symmetry of doped Eu^{3+} ion. In addition, the Judd-Ofelt parameter, transition branch ratios and radiative transition rate were calculated by Judd-Ofelt theory, in order to better understand the radiative properties and the local structure of Eu^{3+} ions in host.

2. Experimental

2.1. Preparation of phosphors

The $CaGd_{2-x}(WO_4)_4$:xEu ($0 \le x \le 1$) phosphors were synthesized via the solid state reaction method. The raw materials Gd_2O_3 (99.95%), Eu_2O_3 (99.95%), $CaCO_3$ (99.9%) and WO_3 (99.9%) were stoichiometrically weighed and ground thoroughly in planetary ball mill for 10 h to obtain homogeneous mixtures. The homogeneous mixtures were dried at 353 K for 10 h and then put into a corundum crucible to calcine at 1123–1323 K in air for 4 h. Finally, the samples were ground slightly to obtain the phosphor powders.

2.2. Characterization

The phases of the phosphors were identified by X-ray powder diffraction (XRPD, D/MAX-2500, Rigaku, Japan) with Cu K_a radiation (λ = 1.5418 Å) at 36 kV tube voltage and 20 mA tube current. The data were collected from 15° to 85° in 2θ range with a scanning step of 0.02°. The microscopic morphology was examined using the scanning electron microscope (SEM, JSM-6360, JEOL, Japan). The excitation and emission spectra were measured by a fluorescence spectrophotometer (F-7000, Hitachi, Japan) equipped with a 150 W Xe lamp as excitation source. The luminescence decay curves were carried out using a FluoroLog-3 fluorescence spectrophotometer (Horiba JY, France). All measurements were carried out at room temperature.

3. Results and discussion

3.1. X-ray powder diffraction analysis and morphology of the phosphors

To determine the crystalline phase and phase formation of $CaGd_2(WO_4)_4$ in different temperature, precursor powders were calcined at 1123, 1173, 1223, 1273 and 1323 K for 4 h, respectively. Fig. 1 shows the XRPD patterns of $CaGd_2(WO_4)_4$ phosphors calcined at various temperatures. It can be seen that the phosphors calcined at 1123 K could be well indexed by the tetragonal scheelite structure, and only three weak peaks corresponding to WO_3 phase were observed. With the calcination temperature increasing, the diffraction peaks of WO_3 become weaker and it is worth noting that the diffraction peaks in the range from 28° to 30° obviously split and broaden as the calcination temperature increasing (Fig. 1 inset). According to the reported literature [21], the above phenomenon is due to the structure transition from a body-centered tetragonal scheelite structure with space group $I4_1/a$, to the monoclinically distorted scheelite structure with space group $I2/b$. When calcination temperature reaches 1273 K, the XRPD pattern of the phosphor

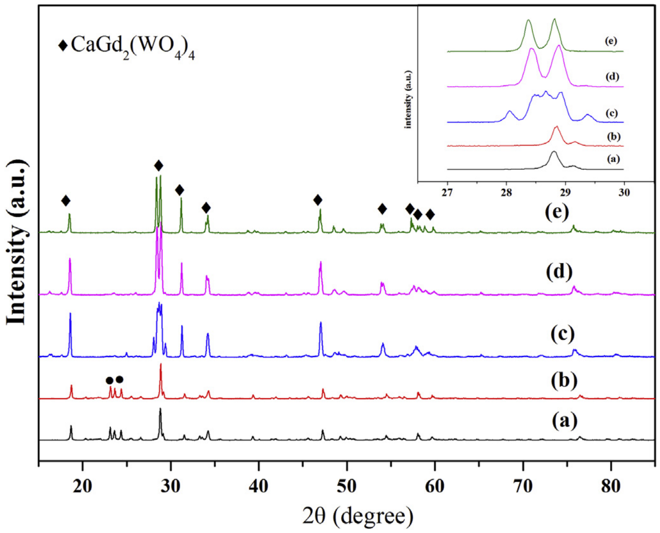

Fig. 1. XRPD patterns of $CaGd_2(WO_4)_4$ phosphors calcined at different temperatures for 4 h (a) 1123 K, (b) 1173 K, (c) 1223 K, (d) 1273 K, (e) 1323 K.