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Investigation of energy transfer mechanism and luminescence properties in Eu^{3+} and Sm^{3+} co-doped $ZnWO_4$ phosphors

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ABSTRACT

A series of $ZnWO_4$:x%Eu^{3+} y%Sm^{3+} phosphors were synthesized by a facile hydrothermal method. The samples were well crystallized in the pure monoclinic wolframite structure with P2/c space group. The produced phosphors have exhibited an intense red emission, moreover, the red emission intensity was enhanced gradually with the increase of the Sm^{3+} content. The energy transfer (ET) of $Sm^{3+}\rightarrow Eu^{3+}$ was proved by the photoluminescence (PL) spectra and decay curves. The average lifetime of Eu^{3+} emission was also decreased from 1.11 ms in $ZnWO_4$:5%Eu^{3+} to 0.90 ms in $ZnWO_4$:5%Eu^{3+}, 2%Sm^{3+}, which demonstrates that there exists ET from Sm^{3+} to Eu^{3+}. These results show that the samarium ions doping greatly enhances the emission dominance of Eu^{3+} at 617 nm.

1. Introduction

In recent years, white light-emitting diodes (w-LEDs) have caused serious concern on account of their long lifetime, small size, high efficiency, energy conservation and environmental friendly [1–3]. At present, The available commercial w-LEDs are made of a blue LED chip combined with yellow phosphors (YAG:Ce^{3+}) [4,5]. However, in this way, the insufficiency of red emitting ingredient lead to the low color rendering index [6]. The mentioned drawback could be addressed by combining a blue chip with red and green phosphors [7], or constructing a UV chip which excites red, green and blue phosphors [8]. Thus, red-emitting phosphors play a significant role in w-LEDs.

The rare earth (RE) ions have been widely applicated in various kinds of display device owing to their unique chemical, electrical and optical properties which derived from the 4f shell of rare earth ions [9–14]. Among the rare earth ions, Eu^{3+} or Sm^{3+} doping phosphors is an essential ingredient to realize the white light. Trivalent europium (Eu^{3+}) is a kind of important red or reddish-orange-light activator which originated from the $^5D_0\rightarrow{}^7F_J$ (J = 0–4) transitions [15–18]. Trivalent samarium (Sm^{3+}) has a fundamental level of $^6H_{5/2}$ and the emitting levels of $^4K_{11/2}$ and $^4G_{5/2}$, which gives the visible orange red emission [19–22].

Recently, the growing interest was focused on the zinc tungstate ($ZnWO_4$) material because of its magnetic, scintillated, catalytic and luminescence properties [23–25]. A great deal of literature has been concerned with the improvement of the catalytic and optical properties of ZnWO4 by doping rare earth ions [26–30]. However, there is very limited report to investigate the luminescence properties and energy transfer mode of rare earth ions co-doped $ZnWO_4$. In this paper, $ZnWO_4$ co-doped with Eu^{3+} and Sm^{3+} has been successfully synthesized via a hydrothermal method. We studied systematically the effects of Sm^{3+} concentrations on luminescence properties of $ZnWO_4:Eu^{3+}$ samples. Meanwhile, the energy transfer mode and process between activators and sensitizers (Sm^{3+}) of the phosphors were also studied in detail.

2. Materials and methods

A series of $ZnWO_4$ phosphors with variable concentrations of Eu^{3+} and Sm^{3+} were synthesized via a facile hydrothermal method. Take $ZnWO_4$:5 mol%Eu^{3+}, 0.6 mol%Sm^{3+} (x = 5,y = 0.6) for example. 4.72 mmol $Zn(NO_3)_2{\cdot}6H_2O$ was dissolved in 5 mL deionized water. To obtain 0.1 mol/L $Eu(NO_3)_3$, 10 mmol Eu_2O_3 was firstly dissolved into nitric acid under continuous stirring. Subsequently, 0.25 mmol $Eu(NO_3)_3$, and 0.03 mmol $Sm(NO_3)_3$ were mixed evenly and were added to the above transparent solution. Then 5 mmol Na_2WO_4 was dissolved in 10 mL deionized water. The Na_2WO_4 aqueous solution was added into the mixed solution drop by drop while stirring, until a white suspension was formed. Meanwhile, the pH value was adjusted to about 6 by dropping sodium hydroxide. After vigorously stirred for 30 min, the resulting suspension was transferred into a Teflon-lined stainless steel autoclave and then the autoclave was sealed and maintained at 180 °C for 12 h. After the autoclave was cooled to room temperature naturally,

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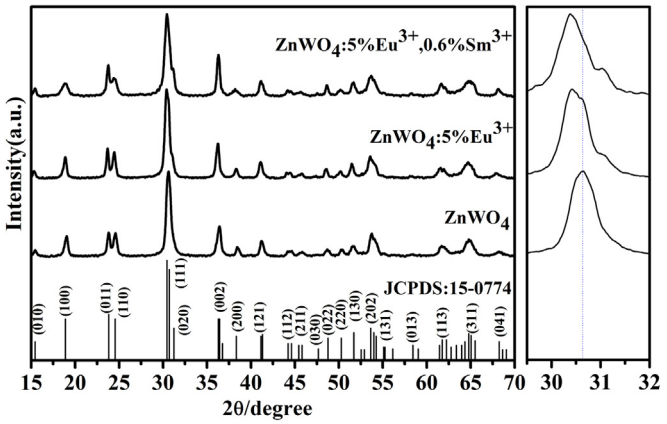

Fig. 1. XRD patterns of $ZnWO_4$, $ZnWO_4$:5% Eu^{3+}, $ZnWO_4$:5% Eu^{3+}, 0.6% Sm^{3+} samples.

the white precipitates were collected by centrifugation, and washed with deionized water and absolute ethanol. Then dried at 70 °C for 12 h in the air. In this way, $ZnWO_4$:5%Eu^{3+}, 0.6%Sm^{3+} sample was synthesized. The $ZnWO_4$:x%Eu^{3+}, y%Sm^{3+} (x = 1,3,5,7,9; y = 0.2,0.4,0.6,0.8,1,2) phosphors were prepared via the similar method.

All the reagents were analytical grade and used without any further purification. The precursor salts and solvent used during the synthesis are $Zn(NO_3)_2{\cdot}6H_2O$ (99%, Sinopharm Chemical Reagent Co., Ltd), Na_2WO_4 (99.5%, Shanghai Bodi Chemical Co., Ltd), Eu_2O_3 (99.99%,), $Sm(NO_3)_3$ (99.99%, Shanghai Diyang Chemical Co., Ltd), HNO_3 (65% ~ 68%, Sinopharm Chemical Reagent Co., Ltd), NaOH (Tianjin Tianli Chemical Reagent Co., Ltd)

The phase purities and crystal structures of all the samples were characterized by X-ray diffractometer (XRD, D/Max-2200, Rigaku Japan) with Cu-Kα radiation (λ = 0.15406 nm) at 40 kV tube voltage, and the samples were scanned at a scanning rate of 8°/min in the 2θ ranging from 15° to 70°. The morphologies were characterized by using transmission electron microscope (TEM, G2-F20-S-TWIN) with a field emission gun operating at 200 kV. X-ray photoelectron spectrum (XPS) was taken on a AXIS SUPRA electron energy spectrometer using Al Kα as the X-ray excitation source. The element contents analyses were carried out with an inductively coupled plasma atomic emission spectrometer (ICP-AES, Agilent 5100, Australia). The excitation spectra, emission spectra and fluorescence decay of the samples were measured by an F-4600 fluorescence spectrometer (Hitachi, Japan). The excitation light source was a 150 W Xe lamp. All the PL spectra were corrected by the spectral response of the experimental setup. All the measurements were conducted at room temperature.

3. Results and discussion

3.1. Characterization of $ZnWO_4$:x% Eu^{3+}, y% Sm^{3+} phosphors

Fig. 1 shows the XRD spectra of $ZnWO_4$ phosphors co-doped with Eu^{3+} and Sm^{3+} ions. It is clearly observed that all the XRD profiles of $ZnWO_4$, $ZnWO_4$:5% Eu^{3+} and $ZnWO_4$:5%Eu^{3+}, 0.6%Sm^{3+} to be well matched with the JCPDS database no. 15-0774, suggesting that as-synthesized product belong to pure monoclinic wolframite structure with P2/c space group. The XRD spectra of $ZnWO_4$:x%Eu^{3+} ($0 < x \leq 9$) and $ZnWO_4$:5%Eu^{3+}, y%Sm^{3+}($0 < y \leq 2$) samples are shown in Fig. S1 and Fig. S2. The ionic radius of Eu^{3+}, Sm^{3+} and Zn^{2+} are 0.095 nm, 0.096 nm and 0.074 nm, respectively, but the ionic radius

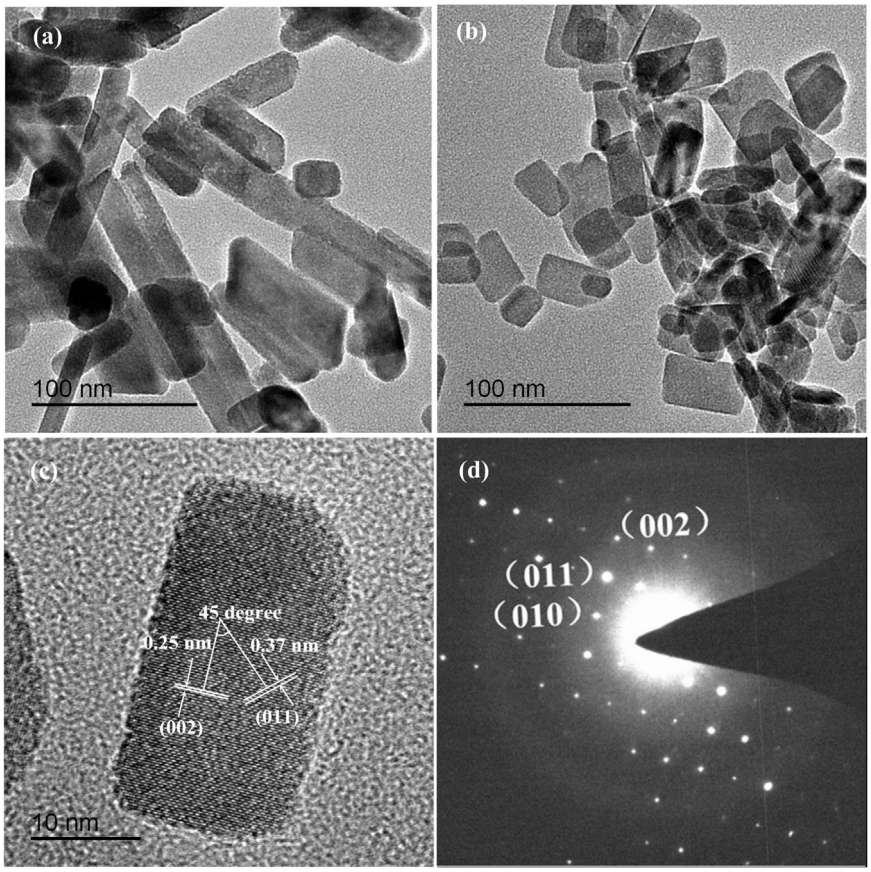

Fig. 2. TEM images of (a) $ZnWO_4$:5%Eu^{3+}, (b) $ZnWO_4$:5%Eu^{3+}, 0.6%Sm^{3+}.(c) HRTEM image and (d) SAED pattern of the individual $ZnWO_4$:5%Eu^{3+}, 0.6%Sm^{3+} nanorod.