



Luminescent properties of Eu^{3+} activated tungstate based novel red-emitting phosphors

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ABSTRACT

A novel red-emission phosphor of Eu^{3+} -doped tungstate was prepared at 950 °C by a modified solid-state reaction. Photoluminescence (PL) results showed that the phosphor can be efficiently excited by irradiation at wavelengths in the near-UV and blue regions of the spectrum. The material has potential application as the fluorescent material for ultraviolet light-emitting diodes (UV-LEDs). The crystallization and particle sizes of the phosphor have been investigated by using powder X-ray diffraction (XRD) and transmission electron microscopy (TEM).

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1. Introduction

White light-emitting diodes (LEDs) have the virtues of high luminous efficiency, energy saving, maintenance and environmental protection. They are believed to be the attractive “green lighting source of the 21st century” and show wide applications and a considerable prospective market [1–3].

Recently, one approach of producing white light has been the combination of a blue InGaN chip ($\lambda_{em} \sim 450\text{--}470\text{ nm}$) with yellow phosphor such as $\text{YAG}:\text{Ce}^{3+}$ [4]. Luminous efficacy and color rendering are two important characteristics of light sources for general lighting [5,6]. However, these approaches lack a red component, and the luminous efficiency and color rendering index of these white LEDs are not very high. With a doped red component, the luminous efficiency and color rendering index of these white LEDs can be improved. The red light-emitting phosphors used for improving Ra and tuning color temperature of the white-light LEDs are still limited commercially to sulfide-based materials such as $\text{CaS}:\text{Eu}^{2+}$, $\text{SrY}_2\text{S}_4:\text{Eu}^{2+}$, and $\text{ZnCdS}:\text{Cu,Al}$ [7,8]. However, there are certain disadvantages to using those sulfide-based materials, such as chemical instability, high FWHM, and low efficiency [9]. Consequently, the study for a stable, inorganic rare earth-based red phosphor with high absorption in the near-UV/blue spectral region is an attractive and challenging research task. In recent years, a great deal of work has been done on Eu^{3+} activation of these hosts. Ren et al. [10] synthesized $(\text{Sr}_{0.85}\text{Zn}_{0.15})_3(\text{PO}_4)_2:\text{Eu}^{3+}$ by a modified solid-state reaction and reported its optical properties. Ternane et al. [11] researched the luminescent properties of Eu^{3+} in calcium hydro-

xyapatite. Therefore, Eu^{3+} doped in phosphate compounds has excellent luminescence.

Tungstate is an important family as the hosts of phosphors that have promising applications in the field of phosphors, optical fibers, scintillators, and laser host materials [12–17], such as CaWO_4 [18], PbWO_4 [19], and ZnWO_4 [20], for their superior luminescence properties. The europium ion is used widely as a luminescent center in many phosphors for the its characteristic red emission corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition [21,22]. The activator Eu^{3+} ions are located at low symmetric sites and at these sites, the excitation probabilities of Eu^{3+} f–f transitions in the near UV region become strong. Furthermore, in the tungstate system, the excitation spectrum of Eu^{3+} at 395 and 465 nm is a line spectrum. Moreover, it is well matched with the LED's violet and blue light emitting. Therefore, the tungstate system of Eu^{3+} is easier to excite by blue and UV LEDs. In many tungstate systems, the concentration of Eu^{3+} can be very high and Eu^{3+} can suffer high power excitation. The phosphor which is excited by Eu^{3+} in tungstate system has lower synthesis temperature, generally between 700 and 1200 °C.

In this paper, we discuss the synthesis and examination of the luminescent properties of Eu^{3+} -doped tungstate phosphor.

2. Experimental procedure

2.1. Sample synthesis

The starting materials were Eu_2O_3 (4 N), La_2O_3 (4 N), $\text{H}_4\text{ON}_{10}\text{O}_{41}\text{W}_{12} \cdot x\text{H}_2\text{O}$ (AR), NH_2CONH_2 (AR), NH_4Cl (AR) (contained Na^+ impurities), and PEG (polyethylene glycol). Eu_2O_3 was dissolved in HNO_3 solution and exactly quantified La_2O_3 , $\text{H}_4\text{ON}_{10}\text{O}_{41}\text{W}_{12} \cdot$

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$x\text{H}_2\text{O}$, NH_2CONH_2 , NH_4Cl , and PEG were ground in an agate mortar at room temperature. Then nitrates solution was introduced and the mixture was carefully ground in an agate mortar at room temperature for about 10 min. Subsequently the white sol was dried in a thermostatic oven at 100°C for about 10 min and an opalescent precursor was attained. The opalescent precursor was transferred to a muffle furnace preheated to 600°C . With boiling, the solution evaporated, giving off much smoke and the entire process lasted for 3–5 min, and a black precursor was obtained. Finally the black precursor was devolved in a muffle furnace preheated to $800\text{--}1000^\circ\text{C}$ (the quadric-sintered temperature) for 3 h, then obtaining the white phosphor powders.

2.2. Sample characterization

The synthesized powders were identified by X-ray powder diffractometer (XRD; Bruker D8, Germany), operating at 40 kV and 40 mA and using $\text{Cu } K\alpha$ radiation ($\lambda=0.15406\text{ nm}$). The XRD patterns were collected in the range $5^\circ \leq 2\theta \leq 80^\circ$. A step size of 0.02° (2θ) was used with scanning speed of $4^\circ/\text{min}$. The morphology and dimension of the product were observed by a transmission electron microscope (TEM), which were taken on a Tecnai G20 (FEI Corporation of Holland) transmission electron microscopy using an accelerating voltage of 200 kV. The emission spectrum was performed by using a Perkin-Elmer

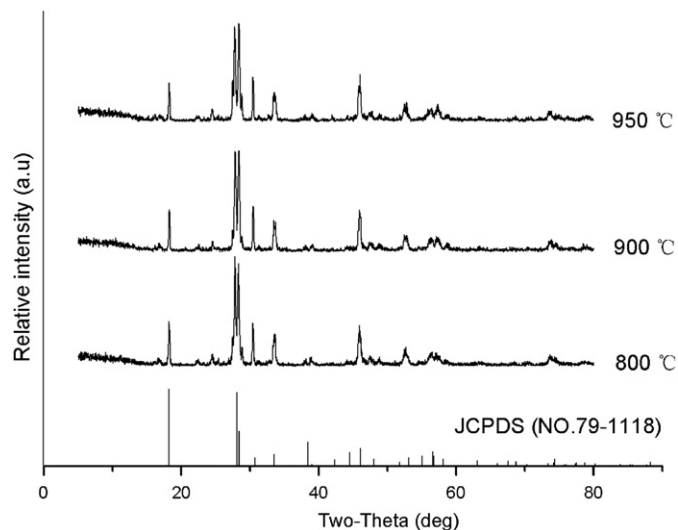


Fig. 1. XRD patterns of powders at different temperature.

LS-55 (Perkin-Elmer Corporation, USA) luminescence spectrophotometer equipped with a xenon-discharge lamp as an excitation source. The excitation and emission slits each were set for 10.0 and 5.0 nm, respectively. All the luminescent properties of the phosphors were studied at room temperature.

3. Results and discussion

3.1. Crystal structural and morphological characterization

The XRD patterns of samples with different temperature concentrations ($800\text{--}950^\circ\text{C}$) have been measured. Fig. 1 shows the XRD patterns of the samples, which suggest that the phase changes occur at $800, 900,$ and 950°C . For the obtained phase, it is observed that there are no peaks corresponding to the raw materials. It is found that the main phase agrees with JCPDS file number 79-1118. From the X-ray diffraction patterns, we can see that different temperature concentrations do not conduce to new phases. This clearly indicates that the crystallization of the $\text{NaLa}(\text{WO}_4)_2$ phosphor is complete and a minute amount of codoped Eu^{3+} has almost no influence on the host structure.

The average structural unit distance was estimated from the full width at half maximum of the diffraction peak by the Scherrer equation [23]: $D = k\lambda/B\cos\theta$, where D is the mean crystallite diameter, k (0.89) is the Scherrer constant, λ is the X-ray wave length (0.15406 nm), and B is the full width half maximum (FWHM) of $\text{NaLa}(\text{WO}_4)_2:\text{Eu}^{3+}$ diffraction peak. The average crystallite size calculated using the most intense reflection at $2\theta=28.38^\circ$, being 30 nm. The morphologies of $\text{NaLa}(\text{WO}_4)_2:\text{Eu}^{3+}$ nanoparticles are clearly demonstrated by TEM image, as shown in Fig. 2. The $\text{NaLa}(\text{WO}_4)_2:\text{Eu}^{3+}$ phosphor particles exhibited some aggregation without any visible admixture of any impurity phases. The grain size of the sample is about 30 nm, which is in full agreement with the data from the XRD patterns.

3.2. Luminescence properties

As is known, the emission spectra are described by $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($J=1, 2, 3$) emission lines of the Eu^{3+} ions with the strong emission for $J=2$ at 616 nm by excitation with 394 nm UV irradiation, which allows that the Eu^{3+} occupies a center of asymmetry in the host lattice [24]. According to the Judd–Ofelt theory, the magnetic dipole transition is permitted. However, the electric dipole transition is allowed only when the Eu^{3+} ion occupies a site without an inversion center and the intensity is

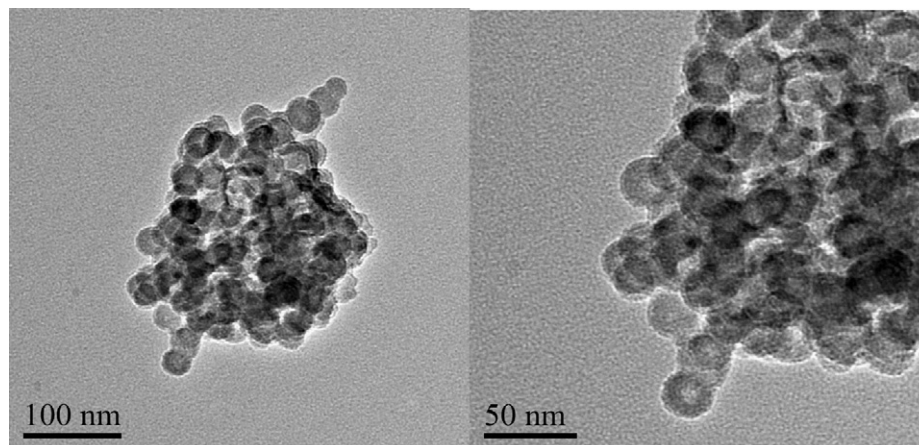


Fig. 2. TEM images of $\text{NaLa}(\text{WO}_4)_2:\text{Eu}^{3+}$ at 100 and 50 nm.

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