



Synthesis and photoluminescence of blue LED excitable $\text{La}_4\text{Ti}_9\text{O}_{24}:\text{Eu}^{3+}$ phosphor for red-light emission



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ABSTRACT

Eu^{3+} activated $\text{La}_4\text{Ti}_9\text{O}_{24}$ phosphors were prepared by firing precursors from sol–gel method. Under the excitation of 465 nm light, the phosphor with optimized concentration at 3% shows strong red light emission peaked at 613 nm with high color purity owing to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission of Eu^{3+} . When adequate amount of either Si^{4+} or Bi^{3+} is incorporated in $\text{La}_4\text{Ti}_9\text{O}_{24}$ host, the photoluminescence intensity of as-prepared $\text{La}_4\text{Ti}_9\text{O}_{24}:\text{Eu}^{3+}$ phosphor can be enhanced by 12% and 19.4%, respectively. As the $(\text{La}_{0.97}\text{Eu}_{0.03})_4\text{Ti}_9\text{O}_{24}$ is pumped with blue-light, high purity red emission with chromaticity coordinates (0.6380, 0.3616) is achieved at the optimized condition. This phosphor might be applied in the solid-state white light emission devices based on blue light-emitting diodes.

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1. Introduction

White light-emitting diodes (W-LEDs) are considered as the next generation solid-state lighting devices owing to the advantages of energy saving, high efficiency, environmental friendly, and long lifetime [1]. At present, most commercial W-LEDs products are fabricated by combining GaN-based blue LED (440–465 nm) and YAG:Ce (YAG) yellow-emitting phosphor. However, this kind of white light has poor color rendering due to the color deficiency in the red region [2]. One way to improve the color rendering index for this GaN chip/YAG combination can be achieved by adding red-light component. The other patterns to generate white light with high color rendering can be achieved through tri-color mix with red, green and blue phosphors as pumped by InGaN-based near-UV LED (370–410 nm), or with red, green phosphors pumped by blue LED [3]. Up to now, most commercial red phosphors are based on Eu^{2+} -doped binary alkaline earth sulfides [4] or Eu^{3+} -doped $\text{Y}_2\text{O}_3\text{S}$ [5], the drawbacks of which are their chemical instability, short lifetime and low efficiency [6]. Therefore, developing of red phosphor with high efficiency, excellent chemical stability, and efficient absorption in blue light (around 460 nm) or near-UV light (around 400 nm) has attracted wide interests.

Recently, lanthanide doped La–Ti–O system, such as $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ [7], $(\text{La}, \text{Pr})_2\text{Ti}_2\text{O}_7$ [8] and $(\text{La}_{0.95}\text{Eu}_{0.05})_2\text{Ti}_2\text{O}_7$ [9], have been investigated for their up-conversion and red-emitting properties. As a member of La–Ti–O system, $\text{La}_4\text{Ti}_9\text{O}_{24}$ consists of a complex network of distorted, octahedral-coordinated titanium sharing corners or edges, linked by two six-coordinated and one eight-coordinated lanthanum ions [10], the La^{3+} sites in this compound have low symmetry, which might be a good host for lanthanide ions. As Eu^{3+} ions usually show a typical $^5\text{D}_0\text{--}^7\text{F}_2$ line-shaped emission around 612 nm when occupying lattice sites without centro-symmetry [11], indicating that $\text{La}_4\text{Ti}_9\text{O}_{24}:\text{Eu}^{3+}$ is suitable to be a red-light-emitting phosphor to compensate red component for white-light.

In this paper, Eu^{3+} activated $\text{La}_4\text{Ti}_9\text{O}_{24}$ red-light emitting phosphor samples, which could be excited by blue light, were prepared by firing precursors from sol–gel method. The photoluminescence of the phosphor and the influence of Si^{4+} or Bi^{3+} incorporation on the emission intensities of the phosphors were investigated.

2. Experimental

Sol–gel method has many advantages over solid-state method, such as good homogeneity, lower sintering temperature, and narrow particle size distribution, which are all beneficial to increase the efficiency of phosphor [12]. $\text{La}_4\text{Ti}_9\text{O}_{24}:\text{Eu}^{3+}$ phosphors were prepared by sol–gel method: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (A.R.) and

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$\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (A.R.) were dissolved in acetic acid (A.R.) to form solution A; $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ (A.R.) was dissolved in anhydrous ethanol (A.R.) to obtain solution B; then stoichiometric amount of solution A was added to solution B under vigorous stirring to produce a clear solution, after that, the as-prepared solution was kept at 80°C to obtain a transparent gel. The obtained gel was heat-treated at 400°C for 2 h, and annealed for 2 h subsequently at a temperature range from 800°C to 1000°C to obtain phosphor samples. Stoichiometric amount of $\text{Si}(\text{OC}_2\text{H}_5)_4$ (A.R.) was added into solution B for the co-doping of Si^{4+} , and the co-doping of Bi^{3+} was achieved by adding stoichiometric amount of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (A.R.) to solution A.

X-ray diffractions (XRD) were examined on Rigaku D/MAX-2500 using $\text{Cu-K}\alpha$ radiation. The morphology of the samples was characterized using a JEOL JEM-2100 transmission electron microscope (TEM) operated at 200 kV. The photoluminescence measurements were carried out using a Shimadzu RF-5301 PC fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source (parameters of excitation and emission slit widths were set to be 1.5 nm). The colorimetry parameters were measured on a PMS-50 Plus UV-Vis-near IR spectro-photocolorimeter (Everfine, China). The lifetimes were measured on a Horiba Jobin Yvon FL3-2-iHR320 fluorescence spectrophotometer. All measurements were carried out at room temperature.

3. Results and discussion

The X-ray diffraction (XRD) patterns of $\text{La}_4\text{Ti}_9\text{O}_{24} \cdot \text{Eu}^{3+}$ powders 2 h after heating the dried gels at different temperature for 2 h are shown in Fig. 1. The diffraction peaks of samples heated at 800°C and 900°C match well with the patterns in JCPDS No. 83-0946 of $\text{La}_4\text{Ti}_9\text{O}_{24}$. As the calcination temperature increases to 1000°C , the intensity of the diffraction peaks increases, and the half width tends to be narrowed, revealing that a high purity, well crystallized $\text{La}_4\text{Ti}_9\text{O}_{24} \cdot \text{Eu}^{3+}$ sample is obtained. Therefore, the sample obtained at the firing temperature of 1000°C is chosen to discuss the luminescence property in the experiment.

As can be seen from the transmission electron microscopy (TEM) image of $\text{La}_4\text{Ti}_9\text{O}_{24} \cdot \text{Eu}^{3+}$ sample in Fig. 2, the particles of the sample are uniform and in a spherical morphology with a mean size of 100 nm, which might be a good candidate to form phosphor

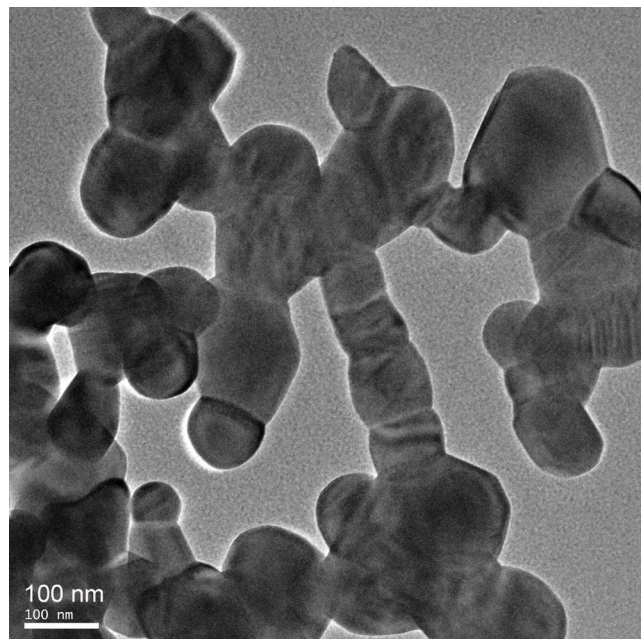


Fig. 2. TEM image of the as-prepared $\text{La}_4\text{Ti}_9\text{O}_{24} \cdot \text{Eu}^{3+}$ particles.

layer with higher packing density and lower surface scattering for manufacturing W-LEDs.

Fig. 3 shows the excitation spectra of $\text{La}_4\text{Ti}_9\text{O}_{24} \cdot \text{Eu}^{3+}$ phosphor in the range of 250–590 nm monitored at 613 nm. The featured excitation lines mainly exist between 380 nm and 600 nm, attributed to transitions from the ${}^7\text{F}_0$ ground state to the excited ${}^5\text{D}_J$ ($J = 0, 1, 2, 3, 4$) and ${}^5\text{L}_6$ levels of the 4f^7 configuration of Eu^{3+} , and the intensities are much higher than that of CTB positioned at 320 nm originated from the charge transfer transition of $\text{O}^{2-} - \text{Eu}^{3+}$ and $\text{O}^{2-} - \text{Ti}^{4+}$. The peaks at 395 nm, 404 nm, and 417 nm are owing to the transitions of ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$. Commonly, the strongest excitation peak for Eu^{3+} is the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$. However, the dominant excitation peaks in the excitation spectra of $\text{La}_4\text{Ti}_9\text{O}_{24} \cdot \text{Eu}^{3+}$ phosphor are ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ electric-dipole transition, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ magnetic-dipole transition and forbidden ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$

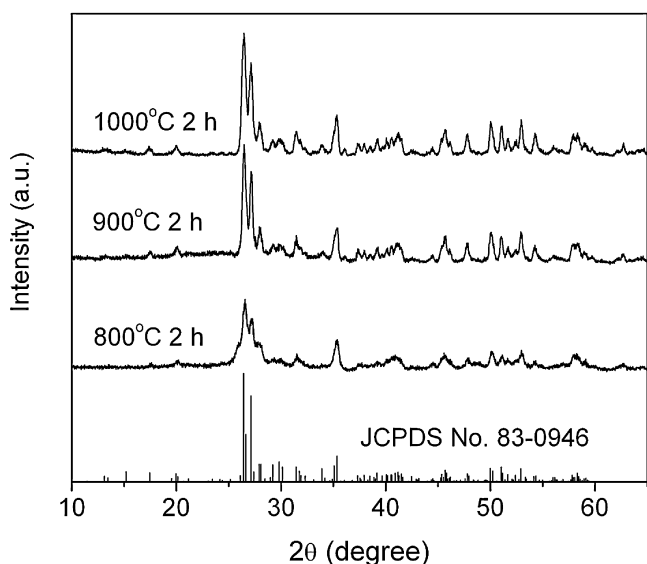


Fig. 1. XRD patterns of as-prepared $\text{La}_4\text{Ti}_9\text{O}_{24}$ powders with JCPDS No. 83-0946.

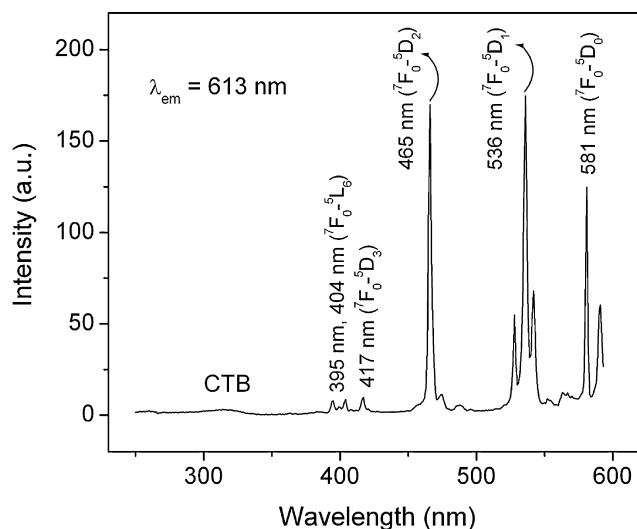


Fig. 3. Excitation spectra of $\text{La}_4\text{Ti}_9\text{O}_{24} \cdot \text{Eu}^{3+}$ at room temperature as monitored at 613 nm.

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