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Low-temperature solid-state synthesis and photoluminescence properties of novel high-brightness and thermal-stable Eu^{3+}-activated $Na_2Lu(MoO_4)(PO_4)$ red-emitting phosphors for near-UV-excited white LEDs

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ABSTRACT

In this paper, novel $Na_2Lu(MoO_4)(PO_4)$:Eu^{3+} phosphors with different Eu^{3+} doping concentrations were synthesized by a low-temperature solid-state method and their crystal structure, morphology, luminescence properties, decay curves and quantum efficiency were investigated in detail. Under near-ultraviolet excitation at 396 nm, all samples exhibited strong red emissions peaking at 593, 616, 655, and 702 nm, corresponding to the characteristic $^5D_0 \rightarrow {}^7F_{1,2,3,4}$ transitions of Eu^{3+} ions. From the concentration-dependent photoluminescence studies of $Na_2Lu(MoO_4)(PO_4)$:Eu^{3+} phosphors, the optimal doping concentration of Eu^{3+} ions was found to be 60 mol%. The as-prepared $Na_2Lu(MoO_4)(PO_4)$:$0.6Eu^{3+}$ sample possessed good colour coordinates of (0.660, 0.338) with high colour purity of 93.5%. More importantly, the emission intensity of $Na_2Lu(MoO_4)(PO_4)$:Eu^{3+} phosphors was about 3.75 and 4.02 times stronger than commercial red phosphors Y_2O_2S:Eu^{3+} and Y_2O_3:Eu^{3+}, respectively. The internal quantum efficiency of $Na_2Lu(MoO_4)(PO_4)$:$0.6Eu^{3+}$ sample was measured to be 73.1%. Furthermore, $Na_2Lu(MoO_4)(PO_4)$:Eu^{3+} exhibited good thermal stability and its emission intensity decreased slightly at temperature above 150 °C. These good results indicate that the $Na_2Lu(MoO_4)(PO_4)$:Eu^{3+} phosphors are very appropriate red-emitting phosphors for applications in near-ultraviolet-excited white light-emitting diodes.

1. Introduction

Nowadays, white light-emitting diodes (white LEDs) are considered to be one of the most important solid-state light sources in lighting industry because of their superior advantages, such as long operating lifetime, low power consumption, and environmental friendliness [1–10]. Currently, white LEDs are generally produced by combining blue LED chips and YAG:Ce^{3+} yellow phosphors, but the obtained white light suffer from high correlated colour temperature (CCT) and poor colour rendering index, limiting their applications in indoor general lighting. An alternative approach for achieve high-quality white LEDs is to combine the near-ultraviolet (near-UV) LED chips with tri-colour (red, green, and blue) phosphors [11–15]. Therefore, there is an urgent need to explore superior tri-colour LED phosphors with effective absorption in the near-UV region, high brightness, and satisfactory stability [16–19].

Trivalent rare-earth (RE^{3+}) doped luminescent materials have attracted extensive attention due to their practical and potential applications in the fields of white LEDs, field-emission displays and so on [20–25]. Among these RE^{3+} ions, Eu^{3+} ion is considered to be one of the most important activators, which can produce intense pure red emission originating from $^5D_0 \rightarrow {}^7F_2$ transition [26–30]. Many studies have been carried out particularly on Eu^{3+} ions doped red-emitting phosphors for white LEDs. On the other hand, the host materials also play an important role in obtaining highly-efficient phosphors. Recently, complex phosphate-molybdates, such as $K_2Bi(MoO_4)(PO_4)$ [31] and $Na_2Gd(MoO_4)(PO_4)$ [32], were proven to be excellent host materials for Eu^{3+} ions, which can give rise to

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efficient red emissions with high internal quantum efficiency (IQE) and good thermal stability.

To the best of our knowledge, so far the luminescent behaviors of the Eu^{3+}-activated $Na_2Lu(PO_4)(MoO_4)$ (NLPM) have not been reported yet. In this paper, we reported on the synthesis, characterization, and optical properties of novel NLPM:Eu^{3+} red-emitting phosphors. These phosphor samples were synthesized by using the high-temperature solid-state reaction technique. The phase structure, microstructure, photoluminescence (PL), decay lifetime, IQE, and thermal stability of resultant samples were studied in detail. The optimal doping concentration of Eu^{3+} ions in NLPM host was found to be 60 mol%. Under the 396 nm near-UV excitation, the CIE coordinates of the NLPM:0.6Eu^{3+} phosphor were determined to be (0.660, 0.338), which were very close to standard red light of (0.67, 0.33). Importantly, the IQE of NLPM:0.6Eu^{3+} phosphor reached as high as 73.1%. Our results revealed that NLPM:Eu^{3+} is a very promising pure red-emitting phosphor for near-UV-excited white LEDs.

2. Experimental

2.1. Preparation of phosphor samples

A series of $Na_2Lu_{(1-x)}(PO_4)(MoO_4)$:$x$$Eu^{3+}$ (hereafter abbreviated as NLPM:$x$$Eu^{3+}$) phosphors have been synthesized by the traditional solid state reaction. Typically, Na_2CO_3 (A.R.), Lu_2O_3 (99.99%), $NH_4H_2PO_4$ (A.R.), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (A.R.) were employed as the raw materials, which were weighed according to the stoichiometric ratio and then ground thoroughly in an agate mortar. Subsequently, the mixtures were shifted into the alumina crucibles and sintered at 600 °C for 24 h in air; then, reground again after cooled down to room temperature and further sintered at 600 °C for another 24 h. After that, the products were slowly cooled down to room temperature and then ground into white powders.

2.2. Characterization

The phase purity and crystal structure of the phosphors were examined by X-ray diffraction (XRD) analysis on Bruker D8 advance with Cu Kα radiation ($\lambda = 1.54056$ Å). The Fourier transform infrared spectroscopy (FTIR) was recorded on Thermo Fisher in10-iz10. The morphology of the phosphors was characterized by using a field-emission scanning electron microscopy system (FE-SEM, MAIA3 TESCAN). The room-temperature PL and PL excitation (PLE) spectra were recorded by utilizing a spectrofluorometer (Edinburgh FS5) with a 150 W continuous-wave Xenon lamp as the excitation source. The temperature ranging from 303 to 503 K was controlled by a homemade temperature stage. The decay curves were measured by an Edinburgh FS5 spectrometer equipped with a pulsed Xenon lamp as the excitation source. The measurement of IQE was performed on Edinburgh FS5 spectrofluorometer equipped with an integrating sphere coated with barium sulfate.

3. Results and discussion

Fig. 1 shows the XRD patterns of NLPM:$x$$Eu^{3+}$ samples with various Eu^{3+} concentrations. However, the JCPDS card of NLPM host cannot be found until now. Ryumin et al. recently reported the XRD profiles of $Na_2MIII(PO_4)(MoO_4)$ (MIII = Tb, Tm, Lu, Er, Ho, and Dy) compounds [33]. It was found that the obtained XRD patterns of NLPM:$x$$Eu^{3+}$ samples matched well with previous report by Ryumin et al. [33] revealing that the Eu^{3+} doping into the NLPM host did not result in significant influence on the crystal structure. Fig. 2 shows the SEM image of the typical NLPM:0.6Eu^{3+} sample. The sample was composed of microparticles with irregular shapes.

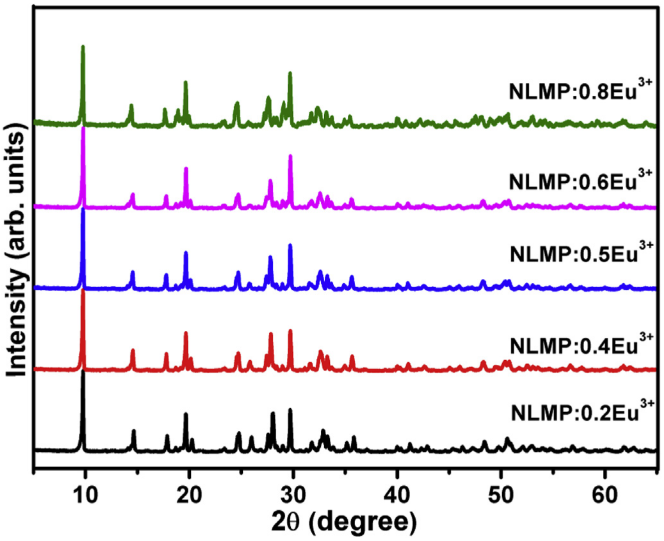

Fig. 1. XRD patterns of NLPM:$x$$Eu^{3+}$ ($x = 0.2$, 0.4, 0.5, 0.6, and 0.8) phosphors.

Fig. 3 shows the FTIR spectrum of NLPM:Eu^{3+} phosphor. The body colors of as-obtained phosphor powders are white. The intense band at 1054 cm^{-1} maybe ascribed to the asymmetric stretching vibration in PO_4 tetrahedron [34]. The band at 912 cm^{-1} was most likely caused by the symmetric stretching vibration of PO_4 assuming the asymmetric MoO_4 tetrahedron. The bands of 774 and 831 cm^{-1} belonged to the Mo—O stretching frequencies in the tetrahedral MoO_4. Another two bands at 577 and 627 cm^{-1} were attributed to bending vibrations of PO_4 tetrahedron. While the other two peaks at 1679 and 3310 cm^{-1} correspond to the bending and stretching vibrations of the O—H bond, respectively, because water might have been absorbed on the surface of the sample [35,36]. The above-mentioned characteristic bands confirmed the simultaneous presence of the phosphate and molybdate groups.

As shown in Fig. 4(a), the PLE spectrum of NLPM:0.6Eu^{3+} phosphors consisted of a broad band in the 250–300 nm region peaking at about 270 nm and several intense sharp lines in the 300–480 nm region, indicating that these phosphors can be effectively excited by UV LED chip (360–400 nm) and blue chip. The broad band was attributed to the CTB transition from the fully filled 2p orbitals of O^{2-} ions to the partially filled 4f orbitals of Eu^{3+} [37,38]. Furthermore, these narrow PLE peaks located at around 365, 378, 383, 396, 418, and 467 nm were attributed to the intra-4f

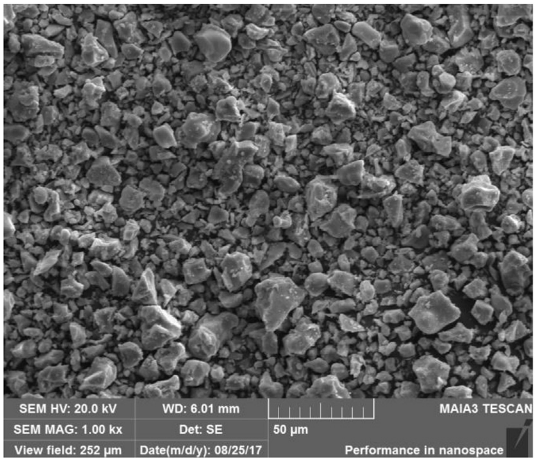

Fig. 2. FE-SEM images of the NLPM:0.6Eu^{3+} sample.