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A novel red phosphor for near UV InGaN light-emitting diode and its luminescent properties

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Abstract

A series of new red phosphors, $NaEu(MoO_4)_{2-2x}(SO_4)_{2x}$, were prepared by the conventional solid state reaction. Their excitation spectra, emission spectra and decay curves were measured at room temperature. When the SO_4^{2-} content is in excess of 20%, other phases appear. With the introduction of SO_4^{2-}, the Mo–O charge transfer band of $NaEu(MoO_4)_{2-2x}(SO_4)_{2x}$ shows red shift, and the excitation intensities of the $4f - 4f$ transitions of Eu^{3+} are strengthened, compared with that of $NaEu(MoO_4)_2$. The single red light-emitting diodes-based these phosphors were fabricated. The light-emitting diode fabricated with the phosphor $NaEu(MoO_4)_{1.80}(SO_4)_{0.20}$ exhibited higher red emission relative to that with $NaEu(MoO_4)_2$. Bright red light can be observed by naked eyes from the light-emitting diode-based $NaEu(MoO_4)_{1.80}(SO_4)_{0.20}$.
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1. Introduction

In recent years, more interests were focused on fabricating the phosphor-converted light-emitting diodes (LEDs) [1–4]. Presently, the emission bands of LED chips are shifted to near UV range around 400 nm since this wavelength can offer a higher efficiency solid-state lighting [5]. However, the main tri-color phosphors for near UV InGaN-based LEDs are still some classic phosphors, such as $BaMgAl_{10}O_{17}:Eu^{2+}$ for blue, $ZnS:(Cu^+, Al^{3+})$ for green, and $Y_2O_2S:Eu^{3+}$ for red [6]. Among these phosphors, the red component $Y_2O_2S: Eu^{3+}$ shows much lower efficiency than that of green and blue phosphors [6]. Therefore, it is urgent to find novel red phosphors, which exhibited intense red emission with strong excitation band around 400 nm, for near UV LED chips.

Double molybdates $ALn(MoO_4)_2$ ($A = Li^+$, Na^+, K^+, Rb^+, Cs^+; Ln = trivalent rare earth ions), which share scheelite-like ($CaWO_4$) iso-structure, show excellent thermal and hydrolytic stability, and are considered to be efficient luminescent hosts [7–10]. In our previous work [11], the luminescent properties of $NaEu(MoO_4)_2$ were investigated, which show intense red emission, appropriate CIE (Commission Internationale de l'Eclairage, International Commission on Illumination) chromaticity coordinates. It's well known that the appropriate phosphors for near-UV LED must show strong and broad absorption around 400 nm firstly. There were two approaches to

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broaden the absorption in this ranged, which had been argued in our previous work [12]. One method is by co-doping Sm^{3+} and Eu^{3+} ions in the phosphor. Another method is to replace the cations or anions of this host compound, then the sub-lattice structure around the luminescent center ions will be expected to be somewhat diverse, hence the excitation band of the phosphor may be broadened.

As a further work, we have synthesized $NaEu(MoO_4)_2$ doped with SO_4^{2-} red phosphors and investigated their luminescent properties in present paper. The anions SO_4^{2-} and MoO_4^{2-} are equivalent, but they show conspicuous difference on the ionic size and the electronic charge density. It is expected that this distinction will result in larger distortion on the sub-lattice structure and thus lead to the broadening and the intensifying of Eu^{3+} absorption near 400 nm. At last the single red LEDs were fabricated using an InGaN LED chip (λ_{em} = 400 nm) precoated with the red phosphor.

2. Experimental

The phosphors $NaEu(MoO_4)_{2-2x}(SO_4)_{2x}$ (x = 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.30, 0.40) were prepared by the solid state reaction technique at high temperature. The starting stoichiometric mixtures were $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (A.R. grade), $NaHCO_3$ (A.R. grade), $(NH_4)_2SO_4$ (A.R. grade), Eu_2O_3 (99.99% purity). They were first ground and pre-fired at 500 °C for 4 h, then heated at 800 °C for 4 h.

The structure of samples was measured by X-ray powder diffraction (XRD) using Cu Kα radiation on a RIGAKU D/max 2200 vpc X-ray diffractometer. Their photoluminescent spectra were recorded on a JOBIN YVON FL3-21 spectrofluorometer and a 450 W xenon lamp was used as excitation source. The luminescence decay curve was obtained from an FLS920 fluorescence spectrophotometer. The emission spectra of the red LEDs were recorded on Labsphere Inc. LED-1100. All the measurements were performed at room temperature.

3. Results and discussion

The XRD patterns of $NaEu(MoO_4)_{2-2x}(SO_4)_{2x}$ (x = 0, 0.10, 0.20, 0.30) are shown in Fig. 1. The curve a shows that $NaEu(MoO_4)_2$ is of single phase and consistent with that given in JCPDS 25-0828 [$Na_{0.5}Gd_{0.5}MoO_4$]. It reveals that $NaEu(MoO_4)_2$ has a scheelite structure [13] with alkali metal ions and rare earth ions disordered in the same site. Mo^{6+} is coordinated by four O^{2-} in a tetrahedral site. Curves b and c are similar with curve a, which shows the phosphors doped with a little SO_4^{2-} are still of scheelite structure. When the SO_4^{2-} content is in excess of 20%, other phases slowly appear (see Fig. 1d). This result shows that a little SO_4^{2-} can be dissolved in the crystal lattice of $NaEu(MoO_4)_2$ to form solid solution. However, due to the difference of the structure between SO_4^{2-} and MoO_4^{2-}, the other phases will appear with the higher content of SO_4^{2-}.

Fig. 2 shows excitation and emission spectra of $NaEu(MoO_4)_{2-2x}(SO_4)_{2x}$ (x = 0, 0.10). The curve a and b are the excitation spectra of $NaEu(MoO_4)_2$ and $NaEu(MoO_4)_{1.80}(SO_4)_{0.20}$ by monitoring emission at 616 nm. The broad band

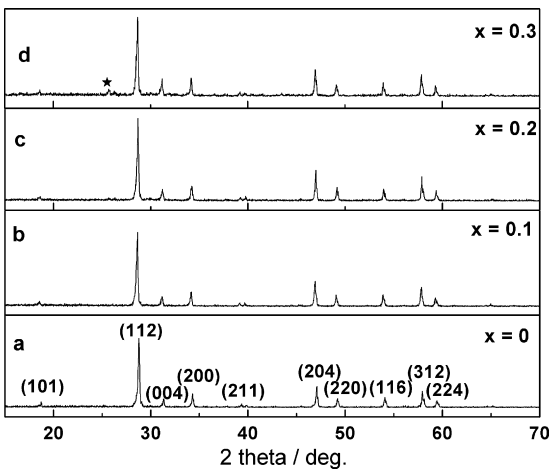

Fig. 1. The XRD patterns of $NaEu(MoO_4)_{2-2x}(SO_4)_{2x}$ (x = 0, 0.10, 0.20, 0.30).

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