

Enhanced photoluminescence of Eu^{3+} -activated calcium molybdate system by co-doping Li^+ and Si^{4+} ions

Xueguang Lu^{*}, Kun Zhao

Research Center of Luminescent Materials, Sichuan Sunfor Lighting Co., Ltd., Chengdu 611731, PR China

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ABSTRACT

A novel red-emitting phosphor $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{Si}_y\text{Mo}_{1-y}\text{O}_4$ ($0.22 \leq x \leq 0.32$, $0 \leq y \leq 0.08$) was synthesized by solid state reaction at 750 °C. The phosphors were characterized by X-ray powder diffraction (XRD) and photoluminescence spectra. The $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{Si}_y\text{Mo}_{1-y}\text{O}_4$ phosphors can be efficiently excited by 395 nm near ultraviolet and 465 nm blue light. The emission spectra exhibit intense red emission with the main emission peak at 617 nm and the chromaticity coordinates locate in the range of $x = 0.667\text{--}0.668$, $y = 0.331\text{--}0.332$ approaching the National Television System Committee (NTSC) standard values ($x = 0.67$, $y = 0.33$). The photoluminescence spectra showed that simultaneously co-doping Li^+ and Si^{4+} ions in Eu^{3+} -activated CaMoO_4 system enhanced luminescence intensity compared with that of $\text{CaMoO}_4:\text{Eu}^{3+}$.

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1. Introduction

Since the first commercial white light emitting diode (LED) based on GaN blue-emitting chip and Ce^{3+} -activated yttrium aluminum garnet ($\text{YAG}:\text{Ce}^{3+}$) yellow phosphor was fabricated in 1997 [1], LEDs have been developed rapidly and have attracted more and more attentions in these days. Owing to having the characteristics of high efficiency, long lifetime and non-pollution, LEDs have been widely utilized in traffic signals, backlight for liquid crystal display (LCD), automobile lamp and especially in solid state lighting [2–4]. However, the white LED assembled by blue-emitting chip and yellow phosphor has poor color rendering index due to deficiencies in red emission, which could not meet the need of those customers who require warm light illumination. To solve this problem, two methods usually were introduced for phosphor-converted LEDs. One approach was to add red-emitting phosphor in the white LED based on blue-emitting chip and yellow phosphor system, the other was to adopt ultraviolet or near-ultraviolet LED chip and blue/green/red tricolor phosphors system. It is evident that red phosphor plays an important role in both ways.

Nowadays some red phosphors, such as molybdates [5–7], tungstates [8], aluminates [9], nitrides phosphors [10,11] and so on, have been developed to overcome the drawback of the poor color rendering index existed in cool white LEDs. Yunsheng Hu et al. disclosed that Eu^{3+} -activated CaMoO_4 phosphor had higher emission intensity and much more stability than sulfide phosphors [5]. However, because of the non-equivalent substitution of Ca^{2+} by

Eu^{3+} ion, it generates vacancy defects that lead to the decrease of emission efficiency. Liu et al. reported that charge compensation could improve the emission intensity of $\text{CaMoO}_4:\text{Eu}^{3+}$ [6]. In this present work, Si^{4+} ion was further incorporated into the $\text{CaMoO}_4:\text{Eu}^{3+}$ system on the basis of adopting Li^+ ion as charge compensator, and the influence of co-doping Li^+ and Si^{4+} ions on luminescence properties of $\text{CaMoO}_4:\text{Eu}^{3+}$ system was investigated.

2. Experimental

2.1. Sample preparation

The $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{Si}_y\text{Mo}_{1-y}\text{O}_4$ samples were prepared by conventional solid state reaction. Analytical Regents of Li_2CO_3 , CaO , SiO_2 , MoO_3 , and Eu_2O_3 (4 N) were taken as raw materials. The stoichiometric of the starting materials were ground and mixed in agate mortar, loaded into alumina crucible, and then heated in muffle furnace at 750 °C for 3 h.

2.2. Characterization

The phase composition of the obtained phosphors was checked by X-ray diffraction (Rigaku D/Max 2500v/pc, $\text{Cu K}\alpha$, 40 kV, 40 mA). Photoluminescence spectra were measured on a Hitachi F7000 fluorescence spectrometer with xenon lamp as excitation source. The excitation slit and the emission slit were both 1 nm. All the measurements were carried out at room temperature.

^{*} Corresponding author. Tel./fax: +86 28 87838194.

E-mail address: nicklxg@163.com (X. Lu).

3. Results and discussion

In order to decrease the vacancy defects originating from non-equivalent substitution of Ca^{2+} by Eu^{3+} ion, a series of $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{MoO}_4$ samples were synthesized using Li^+ ion as charge compensator. The XRD patterns of $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{MoO}_4$ samples are shown in Fig. 1. It can be seen from Fig. 1 that all peaks positions of the samples can be indexed with CaMoO_4 (JCPDS 85-0585), which indicates that the samples contain a single phase having the identical structure to CaMoO_4 , i.e. tetragonal system, space group $I4_1/a(88)$. In addition, the diffraction peaks of the $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{MoO}_4$ ($0.22 \leq x \leq 0.32$) samples shift to higher angle with the augment of the x value obviously, shown in Fig. 2 more clearly, which implies that all the interplanar spacing d_{hkl} values decrease gradually with the increase of the doping concentration of Li^+ and Eu^{3+} ions according to Bragg's law. The ion radius of Li^+ ($r = 92$ pm when CN = 8) and Eu^{3+} ($r = 106.6$ pm when CN = 8) are smaller than that of Ca^{2+} ($r = 112$ pm when CN = 8) [12], thus Li^+ and Eu^{3+} ions have been incorporated into CaMoO_4 lattice successfully.

Fig. 3 shows the excitation spectra of $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{MoO}_4$ ($0.22 \leq x \leq 0.32$) samples. The excitation spectra consist of two different shapes of absorption band, i.e. the board excitation band from 200 nm to 350 nm and narrow sharp peaks in the region of 350–500 nm range. The former board band is attributed to charge transfer (C–T) transitions of $\text{O} \rightarrow \text{Mo}$, while the latter sharp peaks are assigned to intra-configurational $4f-4f$ transitions of Eu^{3+} [13]. For instance, the intense peaks centered at 395 nm and 465 nm correspond to ${}^7\text{F}_0-{}^5\text{L}_6$ and ${}^7\text{F}_0-{}^5\text{D}_2$ transitions of Eu^{3+} , respectively. The intensity of excitation peaks monitored at 617 nm reaches the maximum when x equals to 0.30.

The emission spectra of $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{MoO}_4$ samples ($0.22 \leq x \leq 0.32$) under the excitation of 395 nm were shown in Fig. 4. The emission spectra contain two bands around 592 nm and 617 nm, which are due to ${}^5\text{D}_0-{}^7\text{F}_1$ magnetic-dipole transition and ${}^5\text{D}_0-{}^7\text{F}_2$ hypersensitive forced electric-dipole transition of Eu^{3+} , respectively [14]. The emission intensity of ${}^5\text{D}_0-{}^7\text{F}_1$ transition is much weaker than that of ${}^5\text{D}_0-{}^7\text{F}_2$ transition, which suggests that Eu^{3+} ions occupy the lattice sites without inversion symmetry. Owing to the influence of crystal field, ${}^7\text{F}_1$ and ${}^7\text{F}_2$ energy levels were split into two peaks ${}^5\text{D}_0-{}^7\text{F}_1$ (592 nm, 597 nm), and three peaks ${}^5\text{D}_0-{}^7\text{F}_2$ (609 nm, 614 nm, 617 nm), respectively. When x value is smaller than 0.30, the luminescence intensity of $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{MoO}_4$ samples enhances with the increase of x .

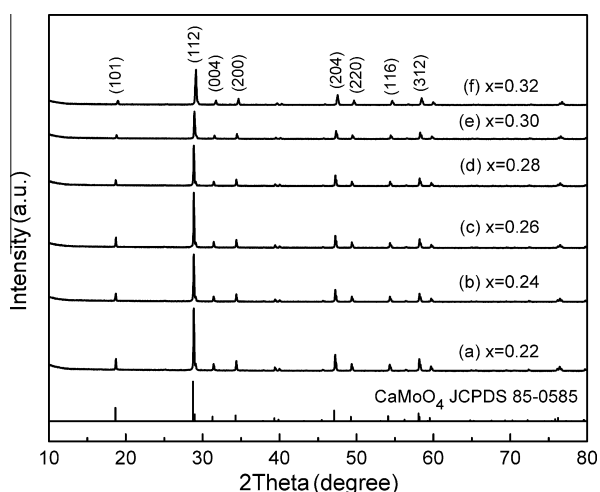


Fig. 1. The XRD patterns of $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{MoO}_4$ samples ($x_a = 0.22$, $x_b = 0.24$, $x_c = 0.26$, $x_d = 0.28$, $x_e = 0.30$, $x_f = 0.32$).

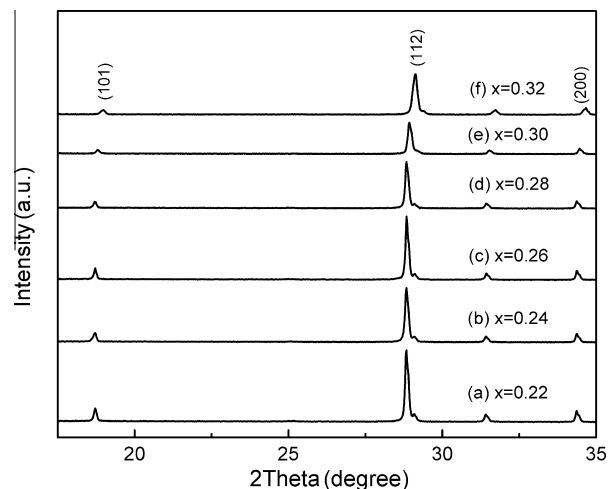


Fig. 2. Magnified XRD patterns of $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{MoO}_4$ ($0.22 \leq x \leq 0.32$) samples in the region from 18° to 35° .

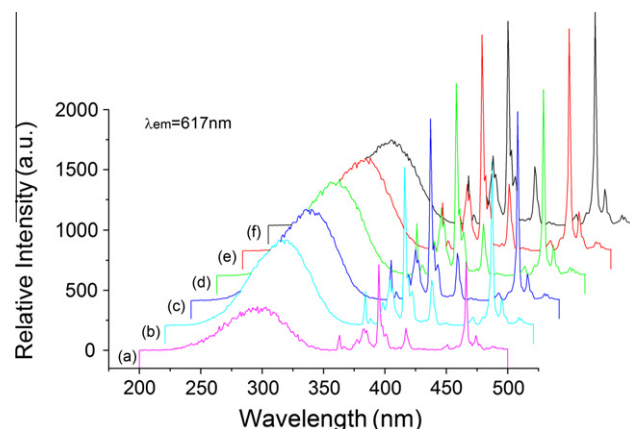


Fig. 3. The excitation spectra of $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{MoO}_4$ samples ($x_a = 0.22$, $x_b = 0.24$, $x_c = 0.26$, $x_d = 0.28$, $x_e = 0.30$, $x_f = 0.32$).

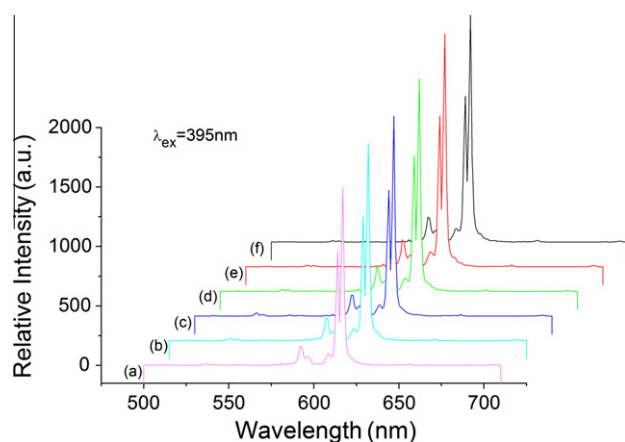


Fig. 4. The emission spectra of $\text{Li}_x\text{Ca}_{1-2x}\text{Eu}_x\text{MoO}_4$ samples ($x_a = 0.22$, $x_b = 0.24$, $x_c = 0.26$, $x_d = 0.28$, $x_e = 0.30$, $x_f = 0.32$).

However, the luminescence intensity decreases if x exceeds 0.30 due to concentration quenching. Therefore, the x value was set 0.30 in the following experiment.

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