Ca$_{1-x}$Mo$_{1-y}$Nb$_y$O$_4$:Eu$^{3+}$: A novel Red Phosphor for White Light Emitting Diodes

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Abstract. Single phase of Ca$_{1-x}$Mo$_{1-y}$Nb$_y$O$_4$:Eu$^{3+}$ (0.18 $\leq$ x $\leq$ 0.26, 0 $\leq$ y $\leq$ 0.07) was synthesized by solid state method. The photoluminescence investigation indicated that Ca$_{1-x}$MoO$_4$:Eu$^{3+}$ (0.18 $\leq$ x $\leq$ 0.26) could be effectively excited by 393nm and 464nm, and it exhibited an intense red emission at 615nm. The incorporation of Nb$^{5+}$ strongly enhanced the emission intensity of $^5$D$_0$-$^7$F$_2$ transition of Eu$^{3+}$ under 393nm and 464nm excitation and the obtained products showed excellent colour purity of which the best chromaticity coordination was x=0.2, y=0.03. The optimal emission intensity excited by 393nm was about 4.2 times higher than that of Y$_2$O$_2$S:0.05Eu$^{3+}$ phosphor. The phosphor could be suitable for the UV LED chips application.

1. Introduction

Phosphor-converted light-emitting diodes (LEDs) technique is an important solid-state illumination [1-4]. In comparison with conventional incandescent and fluorescent lamps, the white LEDs show many advantages such as high luminescent efficiency, long lifetime, compactness, environment friendly and designable features. Generally, the white LED is realized by a combination of an GaN-based blue-LED chip (emitting blue light at 465nm) with a yellow phosphor (i.e. YAG:Ce$^{3+}$ based materials) [5,6]. This method is relatively easy to be fulfilled and the device has been commercialized. However, the scheme of blue LED + yellow phosphor also appears many serious drawbacks such as colour shift, low reproducibility and low colour rendering index (CRI) mainly due to two colour mixing [7,8]. In order to overcome these drawbacks, the white LED has been fabricated by employing blue, green and red emitting multiphase phosphors excited by a near-ultraviolet (UV) InGaN chip recently. The current tri-colour phosphors for near-UV InGaN-LEDs chips are Y$_2$O$_2$S:Eu$^{3+}$ for red, ZnS:(Cu$^+$,Al$^{3+}$) for green, and BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ for blue[9]. Unfortunately, the Y$_2$O$_2$S:Eu$^{3+}$ red phosphor can’t absorb efficiently in near-UV region and its brightness is about 8 times less than that of the green and blue phosphors. As a result, it is necessary to use a phosphor mixture containing 80% red, 10% green and 10% blue in order to obtain good colour rendering. In addition, the lifetime of the Y$_2$O$_2$S:Eu$^{3+}$ is inadequate under extended UV irradiation for its instability. It is the bottleneck for the advancement of white LEDs.

CaMoO$_4$ belongs to the scheelite-like (CaWO$_4$) iso-structure and the central Mo$^{6+}$ is coordinated by four O$^{2-}$ in tetrahedral symmetry (Td) [10]. As reported by Hu et al, CaMoO$_4$:Eu$^{3+}$ shows not only
desirable absorption in near-UV region but also excellent thermal and chemical stability [11]. Thus, CaMoO₄:Eu³⁺ is considered as a promising red candidate that may substitute sulfide phosphors in white LEDs. However, nowadays, the brightness of CaMoO₄:Eu³⁺ is still inadequate for application in white LEDs. Wang et al co-doped Sm³⁺, Bi³⁺, Eu³⁺ in molybdate and obtained an enhanced emission intensity of Eu³⁺ [12,14]. Up to now, there are few investigations considering the substitution for the sites of Mo⁶⁺. According to Ropp [13], the Eu³⁺ in the EuNbO₄ exhibited intense excitation and emission in UV and near-UV region because of the strong coupling between Eu³⁺ and NbO₄ groups [13,15]. Therefore, in this paper, the Ca₁₋ₓMo₁₋ₓNbxO₄:Euₓ³⁺ (0.18 ≤ x ≤ 0.26, 0 ≤ y ≤ 0.07) phosphors are synthesized and the properties of luminescence are investigated in detail.

2. Experimental
The Ca₁₋ₓMo₁₋ₓNbxO₄:Euₓ³⁺ (0.18 ≤ x ≤ 0.26, 0 ≤ y ≤ 0.07) samples were prepared by solid-state reaction in air as follows: The starting materials MoO₃(AR), CaO(AR), Nb₂O₅(AR) and Eu₂O₃(4N) were weighed with the stoichiometric ratios. These powders were blended in an agate mortar. Then, the homogeneous mixture obtained was put into an alumina crucible and calcined in a muffle furnace at 750°C for 4h.

The samples were characterized by powder X-ray diffraction (XRD) using a Rigaku diffractometer with Ni filtered Cu-Kα radiation at room temperature. The photoluminescence spectra were measured by a Xe lamp (FLS-920T) at room temperature.

3. Results and discussion
The X-ray powder diffraction patterns show that all samples are single phase, and their colors are white. As an example, the powder XRD patterns of Ca₀.₈Mo₀.₁₋ₓNbxO₄:Eu₀.₂³⁺ (0 ≤ x ≤ 0.07) are showed in Figure.1, according to the JCPDS card 29-0351, all peaks can be indexed with space group of I41/am (88). No second phases are observed.

Figure.2 shows the excitation spectrum of Ca₀.₈Mo₀.₁₋ₓNbxO₄:Eu₀.₂³⁺ phosphor (λ_em=615nm). The excitation spectrum is divided into two regions: the board absorption band centered at 270nm is assigned to the combination of the charge transfer(CT) transitions of Eu-O and MoO₄²⁻ group and the contribution of the CT transition of MoO₄²⁻ group is dominant in this broad band [12,14]. The weak and narrow peaks above 350nm are assigned to the f-f transitions of Eu³⁺. Among them, the dominant
sharp peaks at 393nm and 464nm are due to \( ^7F_0^\rightarrow{}^5L_6 \) and \( ^7F_0^\rightarrow{}^5D_2 \) transitions of Eu\(^{3+} \), respectively [12,14,15]. Fig.3 shows the emission spectrum of Ca\(_{0.8}\)Mo\(_{0.2}\)Eu\(_{0.2}\)\(^{3+}\) and the variation of the luminescent intensities of the phosphors Ca\(_{1-x}\)Mo\(_{0.4}\)Eu\(_x\)\(^{3+}\) (0.18 \leq x \leq 0.26) with Eu\(^{3+}\) concentration under 393nm excitation. The two red peaks at 615nm and 612nm are assigned to the Eu\(^{3+}\) electric dipole transition of \( ^5D_0^\rightarrow{}^7F_2 \), induced by the lattice sites occupied by Eu\(^{3+}\) without inversion symmetry and the break of parity selection rules [11]. The orange peak at 590nm is weak and ascribed to the Eu\(^{3+}\) magnetic dipole transition \( ^5D_0^\rightarrow{}^7F_1 \), which is insensitive to the site symmetry [11]. It can be found that the emission intensity at 615nm reaches maximum at 20% in Figure.3. So the Eu\(^{3+}\)-doped concentration of Ca\(_{1-x}\)Mo\(_{1-y}\)Nb\(_y\)O\(_4\):Eu\(_x\)\(^{3+}\) (0.18 \leq x \leq 0.26, 0 \leq y \leq 0.07) samples in the following work is fixed to 20%.

![Figure 2](image-url)  
**Figure 2.** the excitation spectrum of Ca\(_{0.8}\)Mo\(_{0.2}\)Eu\(_{0.2}\)\(^{3+}\) phosphor

![Figure 3](image-url)  
**Figure 3.** the emission spectrum of Ca\(_{0.8}\)Mo\(_{0.4}\):Eu\(_{0.2}\)\(^{3+}\) and the variation of the luminescent intensity with Eu\(^{3+}\) concentration in the system Ca\(_{1-x}\)Mo\(_{0.4}\):Eu\(_x\)\(^{3+}\) (0.18 \leq x \leq 0.26).

The excitation spectra of the Ca\(_{0.8}\)Mo\(_{1-x}\)Nb\(_x\)O\(_4\):Eu\(_{0.2}\)\(^{3+}\) (0 \leq x \leq 0.07) samples monitored at 615nm are exhibited in Figure.4. These sharp peaks at about 393nm and 464nm are enhanced obviously by increasing of Nb\(^{5+}\). When the Nb\(^{5+}\)-doped concentration is up to 3%, the intensity of sharp peak at
393nm is the highest and is nearly higher by 75% than that of the original Ca$_{0.8}$MoO$_4$:Eu$_{0.2}^{3+}$ sample (a) while the improvement percent of intensity at 464nm is about 90%. According to Ropp [13], there existed strong coupling between NbO$_4^{3-}$ and Eu$^{3+}$ in some host leading to improvement of emission intensity of Eu$^{3+}$ [16,17,18]. This result indicates that the coupling between NbO$_4^{3-}$ and Eu$^{3+}$ in Ca(Mo,Nb)O$_4$ is strong and the role of Nb$^{5+}$ on increasing the luminescence of CaMoO$_4$:Eu$^{3+}$ is significant. When the concentration of Nb$^{5+}$ is larger than 7\%, the excitation intensities of f-f transitions of Eu$^{3+}$ at 393nm and 464nm are gradually decreased due to the concentration quenching effect. As representatives, the emission spectra of Ca$_{0.8}$Mo$_{1-x}$Nb$_x$O$_4$:Eu$_{0.2}^{3+}$ (0 $\leq$ $x$ $\leq$ 0.07) samples excited at 393nm are exhibited in Figure 5. It is observed that the profiles of these emission lines of all samples are similar to each others. The emission intensity is strongest when Nb$^{5+}$ doped content reaches 3\% and the optimal emission intensity improves 75\% than the original Ca$_{0.8}$MoO$_4$:Eu$_{0.2}^{3+}$ sample (a). This observation is coincident with the results derived from excitation spectra.

**Figure 4.** The excitation spectra of Ca$_{0.8}$Mo$_{1-x}$Nb$_x$O$_4$:Eu$_{0.2}^{3+}$ ($x_a=0$, $x_b=0.01$, $x_c=0.03$, $x_d=0.05$, $x_e=0.07$, $\lambda_{em}=615$nm).

**Figure 5.** The emission spectra of Ca$_{0.8}$Mo$_{1-x}$Nb$_x$O$_4$:Eu$_{0.2}^{3+}$ ($x_a=0$, $x_b=0.01$, $x_c=0.03$, $x_d=0.05$, $x_e=0.07$, $\lambda_{ex}=393$nm).
The relative emission intensities and CIE chromaticity coordinates of $\text{Ca}_{0.8}\text{Mo}_{1-x}\text{Nb}_x\text{O}_4:\text{Eu}^{3+}$ $(0 \leq x \leq 0.07)$ and $\text{Y}_2\text{O}_2\text{S}:0.05\text{Eu}^{3+}$ are listed in Table I. We can find that not only emission intensity but also chromaticity coordinate of $\text{Ca}_{0.8}\text{Mo}_{0.97}\text{Nb}_{0.03}\text{O}_4:\text{Eu}^{3+}$ is the optimum. Compared with the red phosphor $\text{Y}_2\text{O}_2\text{S}:0.05\text{Eu}^{3+}$, the emission intensity of $\text{Ca}_{0.8}\text{Mo}_{0.97}\text{Nb}_{0.03}\text{O}_4:\text{Eu}^{3+}$ is about 4.2 times higher than that of $\text{Y}_2\text{O}_2\text{S}:0.05\text{Eu}^{3+}$ under 393nm excitation which can also be found from their emission spectra (see Figure 6). The CIE chromaticity coordinates of $\text{Ca}_{0.8}\text{Mo}_{0.97}\text{Nb}_{0.03}\text{O}_4:\text{Eu}^{3+}$ is closer to the NTSC standard values than that of $\text{Y}_2\text{O}_2\text{S}:0.05\text{Eu}^{3+}$. These results imply that the luminescent properties of $\text{Ca}_{0.8}\text{Mo}_{0.97}\text{Nb}_{0.03}\text{O}_4:\text{Eu}^{3+}$ may be better than that of $\text{Y}_2\text{O}_2\text{S}:0.05\text{Eu}^{3+}$ when they are applied in UV LED.

![Figure 6](image_url)

**Figure 6.** The emission spectra of $\text{Ca}_{0.8}\text{Mo}_{0.97}\text{Nb}_{0.03}\text{O}_4:\text{Eu}^{3+}$ (a) and $\text{Y}_2\text{O}_2\text{S}:0.05\text{Eu}^{3+}$ (b)

| Phosphor                 | CIE chromaticity coordinates* | Relative intensities of $^5\text{D}_{0}^{-}\text{F}_2(100\%)$ |
|--------------------------|-------------------------------|---------------------------------------------------------------|
| $\text{Ca}_{0.8}\text{MoO}_4:\text{Eu}^{3+}$ | 0.694 0.366 | 100                                                          |
| $\text{Ca}_{0.8}\text{Mo}_{0.99}\text{Nb}_{0.01}\text{O}_4:\text{Eu}^{3+}$ | 0.665 0.334 | 115                                                          |
| $\text{Ca}_{0.8}\text{Mo}_{0.97}\text{Nb}_{0.03}\text{O}_4:\text{Eu}^{3+}$ | 0.662 0.330 | 175                                                          |
| $\text{Ca}_{0.8}\text{Mo}_{0.95}\text{Nb}_{0.05}\text{O}_4:\text{Eu}^{3+}$ | 0.661 0.330 | 155                                                          |
| $\text{Ca}_{0.8}\text{Mo}_{0.93}\text{Nb}_{0.07}\text{O}_4:\text{Eu}^{3+}$ | 0.662 0.330 | 120                                                          |
| $\text{Y}_2\text{O}_2\text{S}:0.05\text{Eu}^{3+}$ | 0.631 0.350 | 41                                                           |

* The NTSC standard values $x=0.67, y=0.33$, the intensity of $\text{Ca}_{0.8}\text{MoO}_4:\text{Eu}^{3+}$ is regarded as 100%.

4. Conclusion

A novel red phosphor $\text{Ca}_{1-x}\text{Mo}_{1-y}\text{Nb}_x\text{O}_4:\text{Eu}^{3+}$ $(0.18 \leq x \leq 0.26, 0 \leq y \leq 0.07)$ has been successfully obtained by solid-state reaction at 750°C for 4h. The x-ray measurements showed that all samples were single phase. The samples $\text{Ca}_{1-x}\text{Mo}_x\text{O}_4:\text{Eu}^{3+}$ $(0.18 \leq x \leq 0.26)$ can be excited efficiently by UV(393nm) and blue(464nm) light and emit the red light at 615nm with line spectra. With the introduction of Nb$^{5+}$, the intensity of emission can be improved and the CIE chromaticity coordinate $(x=0.662, y=0.33)$ was closed to NTSC standard values. Compared with the sulfides phosphors, this
novel phosphor has much stronger emission intensity and better colour purity under the excitation of 393 nm UV light. Most importantly, the novel phosphor is much more stable than sulfide phosphors. All the results indicated that this red phosphor was more suitable for commercial use in near UV InGaN based LEDs.

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