

Luminescence Properties of Tb³⁺, Eu³⁺, Tm³⁺ Co-Doped Na₅La(MoO₄)₄ for White Light-Emitting Diode

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Tb³⁺, Eu³⁺, Tm³⁺ co-doped Na₅La(MoO₄)₄ phosphors were prepared by the conventional solid-state reaction. Under the excitation of UV light, Na₅La(MoO₄)₄:Tm³⁺, Na₅La(MoO₄)₄:Tb³⁺, and Na₅La(MoO₄)₄:Eu³⁺ exhibit the characteristic emissions of Tm³⁺ (¹D₂ → ³F₄, blue), Tb³⁺ (⁵D₄ → ⁷F₅, green), and Eu³⁺ (⁵D₀ → ⁷F₂, red), respectively. By adjusting the doping concentration of rare earth ions in Na₅La(MoO₄)₄:a Tm³⁺, b Tb³⁺, c Eu³⁺, a white emission in a single composition was obtained under the excitation of 362 nm. It might be a promising phosphor for the future applications.

Keywords: Photoluminescence, White Emission, Na₅La(MoO₄)₄:Tb³⁺, Eu³⁺, Tm³⁺, Energy Transfer.

1. INTRODUCTION

Recently, white light-emitting diodes (LEDs) have received lots of attention as a solid-state lighting device because of their advantages such as high energy efficiency, energy savings, and environmental friendliness.^{1–5} There are two methods to generate white light LEDs.⁶ One is the combination of separated red, green, and blue LEDs, which requires complicated electronics and limits its applications.⁷ The other is that the white light is achieved by combining blue LEDs (460 nm) or UV LEDs (300–410 nm) with phosphors. Now the combination of blue LEDs with yellow phosphors (Y₃Al₅O₁₂:Ce³⁺) is the most common method to obtain white light. However, white light produced by blue LED with yellow phosphors (Y₃Al₅O₁₂:Ce³⁺) possesses poor color-rendering index for the absence of red light, which limits the expansion of the LEDs applications.^{8,9} Due to this problem, a UV LED (300–410 nm) coated with tricolor phosphors was introduced, which can provide superior color uniformity with a high color rendering index and excellent quality of light.^{10,11} However, the luminescent efficiency is low in this method, which can be attributed to the strong reabsorption.^{12,13} In addition, the device of white LEDs with multiple emitting components is very complicated

and difficult to be realized. So it is necessary to develop a single-composition white-emitting phosphor which can avoid the above problems.

Recently, the molybdate family has aroused great interest and been chosen as host materials for new luminescent materials which can be activated in the deep UV region (200–250 nm) based on their good stability, low costs, simple synthesis conditions and good luminescence properties.^{14,15,20} However, most of the reports focus on the luminescence properties of Eu³⁺ doped CaMoO₄ for the applications in white LED. Here in this manuscript, we synthesized rare earth ions (Tm³⁺, Tb³⁺, Eu³⁺) singly doped or codoped Na₅La(MoO₄)₄ phosphors, and investigated their luminescence and energy transfer properties in detail. We find that Na₅La(MoO₄)₄:Tm³⁺ phosphors show blue emission under the excitation of 362 nm, which is suitable for excitation of near-UV LED. More interestingly, by codoping with Tm³⁺, Tb³⁺, and Eu³⁺ ions in the Na₅La(MoO₄)₄ host, we realized white emission in a single composition by adjusting the doping concentrations of Eu³⁺ ions.

2. PREPARATION

Powder samples of Na₅La(MoO₄)₄:RE³⁺ (RE = Tm, Tb, Eu) were all prepared by a solid-state reaction from Na₂CO₃, MoO₃, La₂O₃ (AR), Tm₂O₃ (99.99%), Tb₄O₇

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(99.99%), and Eu₂O₃ (99.99%). The powder reagents were mixed in an agate mortar and then adequately triturated for a good mixing. The powder mixtures were then transferred into crucibles and heated at 600 °C in air for 4 h to produce the final samples.

3. CHARACTERIZATION

The structures of samples were characterized by X-ray diffraction (XRD) (Rigaku D/max-rA powder diffractometer with Cu target radiation resource ($\lambda = 1.54078 \text{ \AA}$)). The photoluminescence (PL) excitation and emission spectra were recorded at room temperature using a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The emission spectra of all samples were measured at a fixed band-pass of 0.2 nm with the same instrument parameters.

4. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of Na₅La(MoO₄)₄:Eu³⁺ is shown in Figure 1. It is the XRD pattern of Na₅La(MoO₄)₄, which is consistent with JCPDS 72-2158 (Na₅La(MoO₄)₄, space group I41/a).¹⁶ No other phase can be detected, indicating that the RE³⁺ ions are completely dissolved in the Na₅La(MoO₄)₄ host and the rare earth ions doping did not change the lattice of Na₅La(MoO₄)₄.

Under UV lamp excitation, Na₅La(MoO₄)₄:Tm³⁺, Na₅La(MoO₄)₄:Tb³⁺, and Na₅La(MoO₄)₄:Eu³⁺ samples show bright blue, green, and red luminescence to the naked eye, respectively. Figure 2 shows the PL excitation and emission spectra of Na₅La(MoO₄)₄:0.10Tm³⁺, Na₅La(MoO₄)₄:0.10Tb³⁺, and Na₅La(MoO₄)₄:0.10Eu³⁺ samples, respectively. The excitation spectrum (Fig. 2(a)) of Na₅La(MoO₄)₄:0.10Tm³⁺ monitored at 454 nm shows two peaks at 360 and 207 nm. The first peak is assigned to the ³H₆ → ¹D₂ transition of Tm³⁺ ions.¹⁷ However, the energy of the strong band at 216 nm is higher than

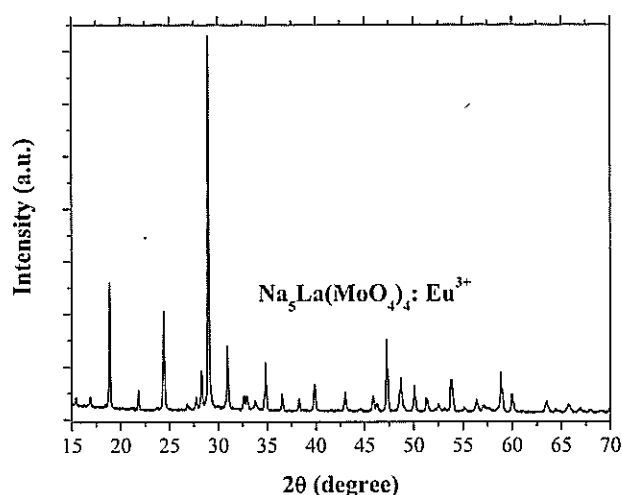


Figure 1. XRD patterns of Na₅La(MoO₄)₄:Eu³⁺.

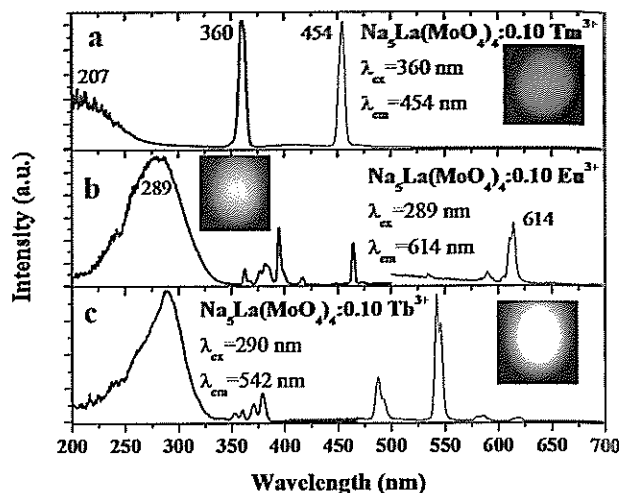


Figure 2. PL excitation (left) and emission (right) spectra of (a) Na₅La(MoO₄)₄:0.10 Tm³⁺, (b) Na₅La(MoO₄)₄:0.10 Eu³⁺, and (c) Na₅La(MoO₄)₄:0.10 Tb³⁺.

3P₂ level of Tm³⁺ at 38193 cm⁻¹ (262 nm) and much lower than its 1S₀ level at 79592 cm⁻¹ (126 nm).¹⁸ So the peak centered at 207 nm was found to be due to absorption of the Na₅La(MoO₄)₄ host lattice. Upon excitation with 360 nm UV light, the Na₅La(MoO₄)₄:0.10Tm³⁺ sample shows a blue luminescence with the peak at 454 nm, and the corresponding emission spectrum consists of the ¹D₂ → ³F₄ transition of Tm³⁺ ions.¹⁹ Figure 2(b) shows the PL spectra of Na₅La(MoO₄)₄:0.10Eu³⁺ sample. The excitation spectrum of Na₅La(MoO₄)₄:0.10Eu³⁺ can be divided into two parts: one part is from 230 to 350 nm with a maximum at 292 nm which is attributed to the CTB of O²⁻-Eu³⁺, and the other part from 350 to 500 nm consists of *f-f* transitions of Eu³⁺ ions. The major red emission peak of Na₅La(MoO₄)₄:0.10Eu³⁺ sample locates at 614 nm together with some weak peaks assigned to the ⁵D₁ → ⁷F₂, ⁵D₀ → ⁷F₀, ⁵D₁ → ⁷F₃, ⁵D₀ → ⁷F₁ in the range from 500 to 600 nm. For the Na₅La(MoO₄)₄:0.10Tb³⁺ sample (Fig. 2(c)), the excitation spectrum consists of a strong band at 263 nm and a weak band at 225 nm, which correspond to the spin-allowed ($\Delta S = 1$) and spin-forbidden ($\Delta S = 0$) components of the 4f⁸ → 4f⁷5d transition, respectively. The emission spectrum of Na₅La(MoO₄)₄:0.10Tb³⁺ is dominated by a green emission at around 550 nm corresponding to the ⁵D₄ → ⁷F₅ transition of Tb³⁺.

On the basis of the above analyses, it can be clearly known that Tm³⁺, Tb³⁺, and Eu³⁺ doped Na₅La(MoO₄)₄ samples can be activated with a 362 nm wavelength which is accessible with near UV-InGaN light emitting devices. Figure 3 shows the CIE coordinates of Na₅La(MoO₄)₄:Tm³⁺, Na₅La(MoO₄)₄:Tb³⁺, and Na₅La(MoO₄)₄:Eu³⁺ samples. The solid-lined triangle depicts the tunable color region of Tm³⁺, Tb³⁺, and Eu³⁺ codoped Na₅La(MoO₄)₄. To obtain white light emission

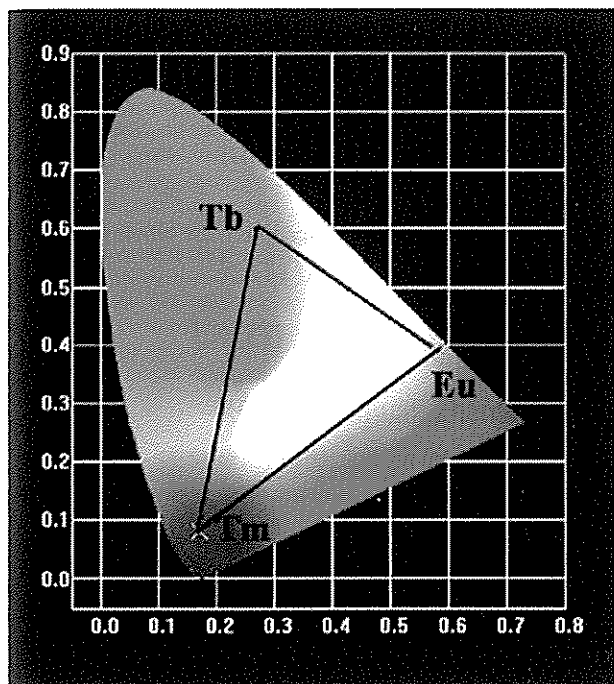


Figure 3. CIE chromaticity diagram for $Na_5La(MoO_4)_4:0.10 Tm^{3+}$, $Na_5La(MoO_4)_4:0.10 Eu^{3+}$, and $Na_5La(MoO_4)_4:0.10 Tb^{3+}$.

in a single component, we codoped Tm^{3+} , Tb^{3+} , and Eu^{3+} ions in the $Na_5La(MoO_4)_4$ host. Figure 4 gives the typical PL emission spectra of the representative $Na_5La(MoO_4)_4:0.10Tm^{3+}$, xTb^{3+} , yEu^{3+} samples under excitation at 362 nm, respectively. Under the excitation of 362 nm, a full-color emission is obtained, resulting from the simultaneous blue, green, and red emission of Tm^{3+} , Tb^{3+} , and Eu^{3+} ions in the $Na_5La(MoO_4)_4$ host. As shown in Figure 4, the cool white color can be realized by adjusting the doping concentrations of rare earth ions. Therefore, a single-composition white-emitting phosphor

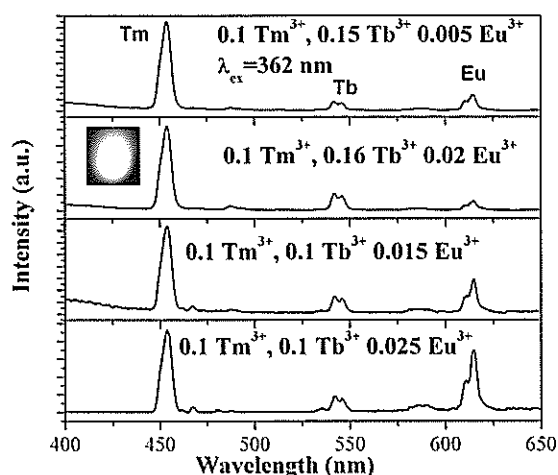


Figure 4. PL emission spectra of $Na_5La(MoO_4)_4:0.10 Tm^{3+}$, xTb^{3+} , yEu^{3+} .

is obtained. This white emission is not a function of the excitation. It is obtained by blending simultaneous blue, green, and red emissions of Tm^{3+} , Tb^{3+} , and Eu^{3+} ions in the $Na_5La(MoO_4)_4$ host. This white emission is dependent on the doping concentrations of rare earth ions.

5. CONCLUSION

In summary, Tm^{3+} , Tb^{3+} , and Eu^{3+} -doped $Na_5La(MoO_4)_4$ phosphors were prepared by a solid-state reaction annealed at 600 °C for 4 h. Under the excitation of UV light, the $Na_5La(MoO_4)_4:Tm^{3+}$, $Na_5La(MoO_4)_4:Tb^{3+}$, and $Na_5La(MoO_4)_4:Eu^{3+}$ phosphors show the characteristic emissions of Tm^{3+} ($^1D_2 \rightarrow ^3F_4$, blue), Tb^{3+} ($^5D_4 \rightarrow ^7F_5$, green), and Eu^{3+} ($^5D_0 \rightarrow ^7F_2$, red), respectively. By codoping Tm^{3+} , Tb^{3+} , and Eu^{3+} into the $Na_5La(MoO_4)_4$ host, a white light emission in a single phase was obtained under the excitation of 362 nm which is accessible with near UV-InGaN LED.

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