Dynamical processes of energy transfer in red emitting phosphor CaMoO₄:Sm³⁺, Eu³⁺

Ye Jin, Zhendong Hao, Xia Zhang, Yongshi Luo, Xiaojun Wang, Jiahua Zhang

Abstract

Upon ⁴K₁₁/₂ excitation of Sm³⁺ at 405 nm, the performance of energy transfer from Sm³⁺ to Eu³⁺ in the red emitting phosphor CaMoO₄:Eu³⁺, Sm³⁺ significantly extends its excitation region for better matching the near-UV LED. Photoluminescence spectra indicate that the energy transfer pathway concerns the relaxation from ⁴K₁₁/₂ to ⁴G₅/₂ of Sm³⁺ and subsequent transfer to ⁵D₀ of Eu³⁺ rather than ⁵D₁ of Eu³⁺. The fluorescent decay pattern of Sm³⁻ ⁴G₅/₂ level in CaMoO₄:0.5% Sm³⁺, 2% Eu³⁺ is studied at 77 K based on the Inokuti–Hirayama formula, revealing an electronic dipole–dipole interaction between Sm³⁺ and Eu³⁺. The coefficient for the energy transfer is obtained to be 8.5 × 10⁻⁶ cm². The fluorescence rise and decay pattern of Eu³⁻ ⁵D₀ level as Sm³⁺ is only excited at 77 K is well described by the dynamical processes of the energy transfer.

1. Introduction

Since the great realization of GaN based blue and/or near-ultraviolet (NUV) light-emitting diode (LED) [1], solid-state lighting based on phosphor converted (pc) white LEDs has attracted much interest because of its great advantages over the conventional incandescent and fluorescent lamps [2–5] in power efficiency, reliability, lifetime and environmental protection [6]. The general strategy of producing white light is to combine a blue LED with a yellow emitting phosphor (YAG:Ce³⁺). This combination leads to high color rendering index (CRI) [7] if red emitting phosphors, which are scarce at present, are obtained. Eu³⁺ doped CaMoO₄ has been investigated as a potential red emitting phosphor for NUV LED based pc-white LEDs because it exhibits more stable physical and chemical properties than the well-known red phosphor, Y₂O₂S:Eu³⁺ [8]. The red emission is originated from ⁵D₀ → ⁷F₂ transition of Eu³⁺ and the NUV excitation performs at around 395 nm through ⁷F₀ → ⁷L₆ absorption of Eu³⁺. Some investigations on enhancing the luminescence intensity of CaMoO₄:Eu³⁺ were reported by introducing Li⁺, Na⁺, K⁺ and Bi³⁺ ions into the phosphor [9–11]. Sm³⁺ was also introduced in CaMoO₄:Eu³⁺, Zhuang et al. compared the luminescence of CaMoO₄:Eu³⁺ with CaMoO₄:Eu³⁺, Sm³⁺ [12]. In our previous work [13], we reported that codoping Sm³⁺ into CaMoO₄:Eu³⁺ can generate additional NUV excitation line at 405 nm, originating from ⁴H₅/₂ → ⁴K₁₁/₂ absorption of Sm³⁺. This behavior is proved to be the result of energy transfer from the ⁴K₁₁/₂ level of Sm³⁺ to the ⁵D₀ level of Eu³⁺. The significance of energy transfer is to extend the excitation lines for effectively covering the NUV LED source in the spectral range of 390–410 nm so as to take advantage of whole spectral components of the LED excitation source. The energy transfer from Sm³⁺ to Eu³⁺ has been also investigated in other red emitting phosphors Na₀.₅Sm₀.₁Eu₀.₄WO₄ [14], NaEu(MoO₄)₂ [15] and other molybdate [16]. However, the physical processes and related parameters in the energy transfer in Sm³⁺ and Eu³⁺ codoped system have not been reported yet.

In this paper, we demonstrate, to our knowledge for the first time, the pathway, interaction mechanism and dynamical processes of energy transfer between Sm³⁺ and Eu³⁺ in CaMoO₄ basing on spectroscopic data and the analysis of rise and decay patterns of fluorescence of Sm³⁺ and Eu³⁺ by using Inokuti–Hirayama formula.

2. Experimental

CaMoO₄:Sm³⁺/Eu³⁺ materials were obtained by solid state reaction in the air as we reported previously [11]. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were...
3. Results and discussion

The powder X-ray diffraction pattern of CaMoO₄:20% Eu³⁺, 0.5% Sm³⁺ is shown in Fig. 1a. All peaks for the as-prepared sample match well with the standard pattern of a pure CaMoO₄ tetragonal structure (JCPDS No. 85-0585). No peaks due to any other phases are detected, indicating the dopant ions do not change the crystal structure of the hosts.

Fig. 1b shows the PLE spectra by monitoring the ⁵D₀ → ⁷F₂ emission of Eu³⁺ at 612 nm in Eu³⁺ singly doped and Eu³⁺ and Sm³⁺ doubly doped CaMoO₄. Both of the samples show a broad PLE band ranging from 200 nm to 325 nm, which is assigned to the combination of the charge transfer transition of Eu³⁺–O²⁻ and MoO₂⁴⁻ group [9]. The sharp PLE line located at around 395 nm is ascribed to the ⁶H₅/₂ → ⁴K₁₁/₂ transition of Sm³⁺, indicating the performance of energy transfer from Sm³⁺ to Eu³⁺.

The diffused reflectance spectra of CaMoO₄:Eu³⁺ and CaMoO₄:Eu³⁺, Sm³⁺ were measured, as shown in Fig. 2. An absorption edge at 300 nm owing to MoO₂⁴⁻ is clearly presented in both the samples and the absorption peaks of intra-4f transitions of Eu³⁺ at 395 and 465 nm, Sm³⁺ at 405 nm are presented. It can be found that the absorption of Eu³⁺ ions enhances with the introduction of Sm³⁺.

The PL spectra of Sm³⁺ singly doped CaMoO₄ under excitation at 405 nm exhibit three characteristic transitions of Sm³⁺: ⁴G₅/₂ → ⁶H₉/₂, ⁴G₅/₂ → ⁶H₇/₂, and ⁴G₅/₂ → ⁶H₅/₂ transitions of Eu³⁺. The other PLE line at 405 nm, which appears only in the samples containing Sm³⁺, is ascribed to the ⁹H₅/₂ → ⁴K₁₁/₂ transition of Sm³⁺, indicating the charge transfer state of Eu³⁺–O²⁻ as illustrated schematically in Fig. 3B. As the ⁴K₁₁/₂ level of Sm³⁺ is excited, it completely relaxes down to the ⁴G₅/₂ state without energy transfer to Eu³⁺. Subsequently, the ⁴G₅/₂ state either returns to the ground states (⁶H₉/₂, ⁶H₇/₂, and ⁶H₅/₂) or transfers its energy to the ⁵D₁ level not the ⁵D₂ level of Eu³⁺ to produce the ⁵D₁ → ⁷F₁ and ⁵D₁ → ⁷F₂ emissions.

The fluorescent decay curves in CaMoO₄:0.5% Sm³⁺, x% Eu³⁺ (x = 0, 1, 2, and 20) are studied for understanding the dynamical processes in energy transfer. The decay curves $I_{Sm}(t)$ for the ⁴G₅/₂ level of Sm³⁺ are measured at 77 K by monitoring ⁴G₅/₂ → ⁶H₉/₂ transitions at 650.5 nm as the ⁴G₅/₂ level is excited by pulsed laser at 563.32 nm, as shown in Fig. 4. The lifetimes of Sm³⁺-⁴G₅/₂ level are obtained using the following expression and listed in Table 1:

$$\tau_{Sm} = \frac{1}{I_{0}} \int_{0}^{\infty} h_{Sm}(t)dt$$

![Fig. 1.](image1.png) **Fig. 1.** (a) X-ray diffraction pattern of CaMoO₄:20% Eu³⁺, 0.5% Sm³⁺; (b) excitation spectra monitoring the ⁵D₀ → ⁷F₂ emission at 612 nm of Eu³⁺ in CaMoO₄:20% Eu³⁺ and CaMoO₄:20% Eu³⁺, 0.5% Sm³⁺.

![Fig. 2.](image2.png) **Fig. 2.** Diffuse reflection spectra of CaMoO₄:Eu³⁺ and CaMoO₄:Eu³⁺, Sm³⁺.
After Sm$^{3+}$ is excited into its $^4G_{5/2}$ state, the energy transfer from donor Sm$^{3+}$ $^4G_{5/2}$ to acceptor Eu$^{3+}$ $^5D_0$ occurs. The depopulation of Sm$^{3+}$ can be described by,

$$n_{\text{Sm}}(t) = e^{-t/\tau_{\text{Sm}}} \phi(t)$$  \hspace{1cm} (2)

where $l_0$ is the fluorescence intensity at the time $t = 0$. As can be seen in Table 1, the lifetimes reduce with increasing Eu$^{3+}$ content $x$, reflecting the effect of energy transfer from $^4G_{5/2}$ level of Sm$^{3+}$ to Eu$^{3+}$. The decay curve is exponential for Sm$^{3+}$ singly doped sample, i.e. $x = 0$, but non-exponential for Sm$^{3+}$ and Eu$^{3+}$ doubly doped sample. For the codoped samples, the non-exponential decay is resulted from the inhomogeneous energy transfer rate [17].

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The nearest Sm³⁺–Eu³⁺ pairs govern the initial energy transfer. This is slightly larger than the calculated value, indicating that the lifetime of 5D₀.

Using Eqs. (2), (3), and (5), we obtain the rate in the sample with 0.5% Sm³⁺ and 2% Eu³⁺ is 2.0 by subtracting the radiative rate from the initial fluorescence decay calculation.

Fig. 6. Rise and decay pattern of fluorescence from 5D₀ of Eu³⁺ in CaMoO₄:0.5% Sm³⁺, 2% Eu³⁺ by pulsed laser at 563.32 nm at 77 K.

1.9 × 10⁴ s⁻¹. Meanwhile, the initial energy transfer rate obtained by subtracting the radiative rate from the initial fluorescence decay rate in the sample with 0.5% Sm³⁺ and 2% Eu³⁺ is 2.0 × 10⁴ s⁻¹, which is slightly larger than the calculated value, indicating that the nearest Sm³⁺–Eu³⁺ pairs govern the initial energy transfer.

Owing to Sm³⁺ → Eu³⁺ energy transfer after pulsed excitation of Sm³⁺→⁴G₅/₂, the populations of Eu³⁺ 5D₀ satisfies the following rate equation:

\[ \frac{dn_{Eu}}{dt} = -n_{Eu}(t)/\tau_{eu} + \omega n_{Sm}(t) \tag{5} \]

where \( n_{eu} \) is the population of the 5D₀ of Eu³⁺, \( \tau_{eu} \) is the intrinsic lifetime of 5D₀. Using Eqs. (2), (3), and (5), we obtain

\[ n_{eu}(t) = e^{-t/\tau_{eu}} \int_{0}^{t} \frac{w f(w)}{w + 1/\tau_{Sm} - 1/\tau_{eu}} \left(1 - e^{-(w-1)/\tau_{Sm}}\right) dw \tag{6} \]

In the case of electric-dipole–dipole interaction with \( m = 6 \), the transfer rate distribution function \( f(w) \) is written as [19]

\[ f(w) = \frac{2\pi n_c \alpha_m^2}{3w^{9/2}} \exp \left( -\frac{4\pi n_c^2 \alpha_m^2}{9w} \right) \tag{7} \]

Using Eq. (6), a numerical calculation for simulating the rise and decay pattern of fluorescence from 3D₀ of Eu³⁺ in CaMoO₄:0.5% Sm³⁺, 2% Eu³⁺ is perfectly performed, as shown in Fig. 6. In the calculation, \( \tau_{eu} = 470 \mu s \) is applied, which is obtained from the exponential decay pattern of 3D₀ → 7F₂ fluorescence in 2% Eu³⁺ singly doped CaMoO₄. As one can see, the decay curve of Eu³⁺ 5D₀ level is composed of a rising edge starting from zero and a falling decay. It indicates that the populations of 5D₀ of Eu³⁺ are completely fed by Sm³⁺→⁴G₅/₂ through energy transfer.

4. Conclusions

In CaMoO₄:Sm³⁺, Eu³⁺, when the ⁴K₁₁/₂ of Sm³⁺ is excited, the excited ⁴K₁₁/₂ relaxes down to the ⁴G₅/₂ of Sm³⁺ itself rather than transfers to Eu³⁺. The Sm³⁺ → Eu³⁺ energy transfer performs through the pathway from Sm³⁺→⁴G₅/₂ state to Eu³⁺ 5D₀ state rather than Eu³⁺ ⁴D₁ state. The electronic dipole–dipole interaction between Sm³⁺ and Eu³⁺ governs the transfer dynamical processes with the coefficient for the energy transfer of 8.5 × 10⁻⁴ s⁻¹ cm⁶. As the ⁴K₁₁/₂ of Sm³⁺ is only excited, the fluorescent rise and decay pattern of Eu³⁺ 5D₀ state is well simulated based on Sm³⁺ → Eu³⁺ dipole–dipole energy transfer model.

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