Energy transfer in $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}, \text{Pr}^{3+}$ and $\text{CaMoO}_4:\text{Sm}^{3+}, \text{Eu}^{3+}$ phosphors

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**Abstract**

Non-radiative energy transfers (ET) from Ce$^{3+}$ to Pr$^{3+}$ in $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}, \text{Pr}^{3+}$ and from Sm$^{3+}$ to Eu$^{3+}$ in $\text{CaMoO}_4:\text{Sm}^{3+}, \text{Eu}^{3+}$ are studied based on photoluminescence spectroscopy and fluorescence decay patterns. The result indicates an electric dipole–dipole interaction that governs ET in the LED phosphors. For Ce$^{3+}$ concentration of 0.01 in YAG:Ce$^{3+}, \text{Pr}^{3+}$, the rate constant and critical distance are evaluated to be $4.5 \times 10^{-36} \text{ cm}^6 \text{s}^{-1}$ and 0.81 nm, respectively. An increase in the red emission line of Pr$^{3+}$ relative to the yellow emission band of Ce$^{3+}$, on increasing Ce$^{3+}$ concentration is observed. This behavior is attributed to the increase of spectral overlap integrals between Ce$^{3+}$ emission and Pr$^{3+}$ excitation due to the fact that the yellow band shifts to the red spectral side with increasing Ce$^{3+}$ concentration. In CaMoO$_4$:Sm$^{3+}, \text{Eu}^{3+}$, Sm$^{3+}$–Eu$^{3+}$ transfer occurs from $^4\text{G}_{5/2}$ of Sm$^{3+}$ to $^5\text{D}_0$ of Eu$^{3+}$. The rate constant of $8.5 \times 10^{-36} \text{ cm}^6 \text{s}^{-1}$ and the critical transfer distance of 0.89 nm are evaluated.

**1. Introduction**

White light-emitting diodes (LEDs) have attracted much interest in recent years for their significant potentials in solid-state lighting of next generation. At present the main strategy for producing white LEDs is to combine blue and/or near UV (NUV) LED with phosphors. The combination of blue LED with the yellow emitting $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ (YAG:Ce$^{3+}$) phosphor is a general way to produce white light. YAG:Ce$^{3+}$ can effectively absorb blue light and subsequently emit yellow light, originating from the transition from the lowest 5d state to $^2\text{F}_{3/2}$ and $^2\text{F}_{7/2}$ ground states of Ce$^{3+}$ [1,2]. However, YAG:Ce$^{3+}$ has relatively weak emission in the red spectral region, leading to low color rendering of white LEDs. To enhance the red component, Mueller-Mach et al. [3] added Pr$^{3+}$ to YAG:Ce$^{3+}$ and consequently observed a sharp red line at about 608 nm, originating from $^1\text{D}_2$ → $^1\text{H}_4$ transition of Pr$^{3+}$, meaning the performance of energy transfer (ET) from Ce$^{3+}$ to Pr$^{3+}$ in YAG. Subsequently, YAG:Ce$^{3+}, \text{Pr}^{3+}$ attracted many investigations [4–7].

The combination of a NUV LED with RGB phosphors is another alternative to produce white light, which may provide a high color rendering and stable color point against forward current. Among the RGB phosphors, red-emitting phosphors are scarce at present. Eu$^{3+}$ doped CaMoO$_4$ has been investigated as a potential red-emitting phosphor because it exhibits more stable physical and chemical properties than the well-known red phosphor $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$. The red emission is originated from $^5\text{D}_0$ → $^3\text{F}_2$ transition of Eu$^{3+}$ and the NUV excitation performs at around 395 nm through $^7\text{F}_0$ → $^7\text{F}_0$ absorption of Eu$^{3+}$. Some investigations on enhancing the luminescence intensity of CaMoO$_4$:Eu$^{3+}$ were reported by introducing Li$^+$, Na$^+$, K$^+$ and Bi$^{3+}$ ions into the phosphor [8–10]. In our previous work [11], we added Sm$^{3+}$ to CaMoO$_4$:Eu$^{3+}$ to generate additional NUV excitation line at 405 nm, originating from $^4\text{H}_{15/2}$ → $^2\text{F}_{7/2}$ absorption of Sm$^{3+}$ based on the performance of ET from Sm$^{3+}$ to Eu$^{3+}$. The significance of the transfer is to extend the excitation lines in the spectral range 390–410 nm so as to take advantage of all spectral components of the NUV LED excitation source. Energy transfer from Sm$^{3+}$ to Eu$^{3+}$ was also observed in other red-emitting phosphors Na$_{0.5}\text{S}-\text{Mo}_2\text{O}_4\cdot\text{TiO}_2\cdot\text{Eu}_2\text{O}_3$ [12], Na$_{0.5}\text{S}-\text{Mo}_2\text{O}_4\cdot\text{TiO}_2\cdot\text{Eu}_2\text{O}_3$ [13] and other molybdate [14].

In this paper, we demonstrate energy transfer dynamical processes in YAG:Ce$^{3+}, \text{Pr}^{3+}$ and CaMoO$_4$:Sm$^{3+}, \text{Eu}^{3+}$ based on experimental measurements of photoluminescence (PL) and fluorescence decay curves.

**2. Experimental**

The powder samples have been prepared by conventional solid-state reaction. For the preparation of YAG:Ce$^{3+}, \text{Pr}^{3+}$, phosphor, Y$_2$O$_3$, CeO$_2$, Al$_2$O$_3$ and Pr$_2$O$_3$ are mixed in 1 M $(Y_{1-x-y}, Ce_x, Pr_y)Al_2O_3$ (x, y represent the concentration of Ce$^{3+}$ and Pr$^{3+}$, respectively) and 3 wt% BaF$_2$ was added as the flux. After a good mixing in an agate mortar, the mixture was sintered...
at 1500 °C for 3 h under a reducing atmosphere. CaMoO4:Sm3+/Eu3+ phosphors were obtained by solid-state reaction in air as reported previously [10]. The structure of final products is characterized by powder X-ray diffraction (XRD). PL spectra are measured with a Hitachi Spectra-fluorometer (F-4500). The decay of fluorescence with lifetime less than 1 μs is measured by an FL920 fluorometer (Edinburgh Instruments, Livingston, UK) with a hydrogen flash lamp (nF900; Edinburgh Instruments). In the measurements of fluorescent decay with lifetime longer than 1 μs, an optical parametric oscillator (OPO) is used as an excitation source. The signal is detected by a Tektronix digital oscilloscope (TDS 3052).

3. Results and discussion

3.1. Energy transfer in YAG:Ce3+, Pr3+

Fig. 1 shows the decay curve of yellow fluorescence of Ce3+ in sample series A (Y0.99−xCe0.01Prx)3Al5O12. The decay is measured by monitoring at 530 nm on 340 nm pulsed excitation. The decay changes from exponential to non-exponential patterns with increasing x, reflecting the effect of Ce3+-Pr3+ ET. The ET pathway is concomitantly considered to start from the lowest 5d state of Ce3+ to the 1D2 state of Pr3+. Based on the Ce3+ and Pr3+ energy level diagrams, a radiative ET seems to be possible. However, we cannot observe the red line in a blend of YAG:Ce3+ and YAG:Pr3+ phosphors, indicating that ET takes place rather by non-radiative interaction, as suggested by Yang and Kim [6]. The normalized intensity of donor fluorescence can be written as

\[ I_d(t) = I_{d0}f(t) \]  

where \( I_{d0} \) is the decay function of donors in the absence of acceptors and the function \( f(t) \) characterizes loss of excited donors due to one way ET to the acceptors. If the ET rate between a donor and an acceptor is proportional to an inverse power of the distance \( r \), written as \( t^{-m} \), according to the Inokuti–Hirayama [15] formula, we have

\[ f(t) = \exp[-\frac{4}{3} \pi \Gamma (1 - \frac{3}{m}) n_A \alpha^{3/m} t^{3/m}] \]

where \( \alpha \) is a rate constant for ET; \( m = 6, 8 \) and \( 10 \) are the coefficients for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interaction, respectively and \( n_A \) is the number of acceptor ions per unit volume. From Eqs. (1) and (2), \( \ln[\ln(I_{d0}(t)/I_d(t))] \) acts as a linear function of \( \ln(t) \) with a slope of \( 3/m \), and \( \ln[I_d(t)/I_{d0}(t)] \) is proportional to \( t^{2/m} \) with a slope of \( 4\pi \Gamma (1 - \frac{3}{m}) n_A \alpha^{3/m} t^{3/m}/3 \). Labeling the 5d state of Ce3+ by 1, the \( \log-\log \) plot of \( \ln[I_d(t)/I_{d0}(t)] \) vs. \( t \) for sample \( (Y_{0.99−x}Ce_{0.01}Pr_x)Al_5O_{12} \) with \( x = 0.01 \) and 0.02, as shown in Fig. 3. The best fitting to each of the two curves yields a transfer constant \( \alpha = 4.5 \times 10^{-36} \text{ cm}^6 \text{s}^{-1} \) for Ce3+-Pr3+ ET in YAG with Ce3+ concentration of 0.01. In the fitting \( n_A \), i.e. the number density of Pr3+, is given by \( xN_Y \) with \( N_Y = 1.38 \times 10^{22} \text{ cm}^{-3} \) being the number of Y sites per unit volume in YAG. Using the value of \( \alpha \) the critical ET distance \( r_0 \) (the spatial separation between a donor and an acceptor, where the ET rate \( \alpha/r_0^6 = 1/\tau_{10} \)) is calculated to be about 0.81 nm. In the calculation, the intrinsic lifetime \( \tau_{10} \) is 61 ns determined in 0.0005 Ce3+ lowly doped YAG, which exhibits a pure exponential decay. In Fig. 2 there is an increase in slope below 20 ns, forming a crossover [16]. As we know, Eq. (2) is obtained by assuming the

![Fig. 1](image1.png)  

**Fig. 1.** Decay curves of yellow fluorescence in \( (Y_{0.99−x}Ce_{0.01}Pr_x)Al_5O_{12} \) for \( x = 0, 0.005, 0.01 \) and 0.02.

![Fig. 2](image2.png)  

**Fig. 2.** \( \log-\log \) plot of \( \ln[I_d(t)/I_{d0}(t)] \) vs. \( t \) for sample \( (Y_{0.99−x}Ce_{0.01}Pr_x)Al_5O_{12} \) with \( x = 0.02 \). The solid line indicates the fitting behaviors.

![Fig. 3](image3.png)  

**Fig. 3.** Plotted \( \ln[I_d(t)/I_{d0}(t)] \) vs. \( t^{1/2} \) for the samples \( (Y_{0.99−x}Ce_{0.01}Pr_x)Al_5O_{12} \) with \( x = 0.01 \) and 0.02. The solid line indicates the fitting behaviors.
nearest distance between a donor and an acceptor to be 0, leading to an infinite initial ET rate. Hence, Eq. (2) is not applicable at short times, which is less than 20 ns in the present sample.

To improve the color rendering of white LED, it was observed [5,6] that further increasing Pr3+ concentration for obtaining sufficient red components, however, leads to reduction of the red line due to Pr3+-Pr3+ self-quenching [17,18]. Fig. 4 shows the PL spectra of sample series B (Y0.995–yCe0.005)3Al5O12 with Pr3+ concentration fixed at 0.005 and various Ce3+ concentration y in the range 0–0.02, where intensity of the yellow emission band of Ce3+ is normalized. It can be seen that the intensity ratio of red to yellow emission (R/Y) monotonously grows up with increasing y, showing a way to improve the red component of the phosphor. In view of small changes of the red fluorescence lifetimes with increasing y, the enhanced red line is an indication of increased macroscopic Ce3+-Pr3+ ET rate. One can find the existence, in connection with the enhancement of the R/Y ratio, of a redshift of the yellow PL band with increasing Ce3+ concentration, as has been observed in Ce3+ singly doped YAG [19]. The redshift enhances the spectral distribution of the yellow band at the position of the red line. As a result, we suggest that the redshift is favourable for effectively increasing the spectral overlap integrals between the yellow emission band and the red absorption line, and therefore enhancing the ET rate. In the case of much narrower red line than the yellow band, their spectral overlap integral is proportional to the spectral intensity of the yellow band at the red line site, denoted by YR. The R/Y ratio and YR approximately satisfy a proportional relationship, as shown in Fig. 5.

3.2. Energy transfer in CaMoO4:Sm3+, Eu3+

The PL spectra of Sm3+ singly doped CaMoO4 under excitation at 405 nm exhibit three characteristic transitions of Sm3+: 4G5/2→4H9/2 (561 nm), 4G5/2→4H7/2 (596 nm, 604 nm) and 4G5/2→4H9/2 (642 nm), as shown in Fig. 6(a). The PL spectra of Eu3+ singly doped CaMoO4 under excitation at 395 nm consist of series of characteristic lines of Eu3+ originating from the transitions of 5D0→7F1 at 534 nm, 5D0→7F1 at 590 nm and
of Sm $^{3+}$ to 5D$_0$ level of Eu $^{3+}$, decay of 4G$_{5/2}$
level is excited at 561 nm in CaMoO$_4$: 0.5% Sm$^{3+}$, 2% Eu$^{3+}$. The ln–ln
plot of ln[I$_{4G5/2}$(t)]/ln[I$_{30}$(t)] vs. t shows a slope close to 3/6, indicating
an electric dipole–dipole energy transfer with $m$=6. Fig. 8 shows the plot of ln[I$_{5D1}$(t)]/ln[I$_{30}$(t)] vs. t$^{1/2}$. The slope of linear pattern yields
x to be $8.5 \times 10^{-40}$ cm$^6$ s$^{-1}$. The critical ET distance of 0.89 nm is
evaluated. In the calculation, I$_{30}$(t) has an exponential decay of the
form exp(-t/$\tau_{30}$), where $\tau_{30}$ is 595 $\mu$s as obtained in CaMoO$_4$: 0.5% Sm$^{3+}$.

4. Conclusion

Non-radiative energy transfers (ET) from Ce$^{3+}$ to Pr$^{3+}$ in
Y$_3$Al$_2$O$_{12}$:Ce$^{3+}$, Pr$^{3+}$ and from Sm$^{3+}$ to Eu$^{3+}$ in CaMoO$_4$:Sm$^{3+}$, Eu$^{3+}$ are both governed by an electric dipole–dipole interaction. For Ce$^{3+}$ concentration of 0.01, the corresponding rate constant and critical distance are evaluated to be 4.5 $\times 10^{-40}$ cm$^6$ s$^{-1}$ and 0.81 nm, respectively, for Ce$^{3+}$–Pr$^{3+}$ ET in YAG. An increase in red/yellow ratio on increasing Ce$^{3+}$ concentration is observed. This behavior is attributed to the increase of spectral overlap integrals between Ce$^{3+}$ emission and Pr$^{3+}$ excitation due to the fact that the yellow band shifts to the red side with increasing Ce$^{3+}$ concentration while the red line does not move.

In CaMoO$_4$:Sm$^{3+}$, Eu$^{3+}$ phosphor, Sm$^{3+}$–Eu$^{3+}$ transfer occurs from $^4G_{5/2}$ of Sm$^{3+}$ to $^5D_0$ of Eu$^{3+}$. The transfer rate constant of 8.5 $\times 10^{-40}$ cm$^6$ s$^{-1}$ and the critical transfer distance of 0.89 nm are evaluated.

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References