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Interionic energy transfer in Y₃Al₅O₁₂:Ce³⁺, Pr³⁺ phosphor

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We present an investigation of dynamical processes of nonradiative energy transfer (ET) between Ce³⁺ and Pr³⁺, and between Pr³⁺ ions in Y₃Al₅O₁₂:Ce³⁺, Pr³⁺ phosphor. Photoluminescence spectroscopy and fluorescence decay patterns are studied as a function of Pr³⁺ and Ce³⁺ concentrations. The analysis based on Inokuti–Hirayama model indicates that the ET from the lowest 5d state of Ce³⁺ to the 1D₂ state of Pr³⁺, and the quenching of the 1D₂ state through a cross relaxation involving Pr³⁺ ions in the ground state are both governed by electric dipole–dipole interaction. An increase in the Ce³⁺–Pr³⁺ ET rate followed by the enhanced red emission line of Pr³⁺ relative to the yellow emission band of Ce³⁺ on only increasing Ce³⁺ concentration is observed. This behavior is attributed to the increase in the spectral overlap integrals between Ce³⁺ emission and Pr³⁺ excitation due to the fact that the yellow band shifts to the red spectral side with increasing Ce³⁺ concentration while the red line does not move. For Ce³⁺ concentration of 0.01 in YAG:Ce³⁺, Pr³⁺, the rate constant and critical distance are evaluated to be 4.5×10⁻³⁶ cm⁶ s⁻¹, 0.81 nm for Ce³⁺–Pr³⁺ ET and 2.4×10⁻³⁸ cm⁶ s⁻¹, 1.30 nm for Pr³⁺–Pr³⁺ ET. Spectroscopic study also demonstrates a pronounced ET from the lowest 4f⁵d of Pr³⁺ to the 5d of Ce³⁺. A proportional dependence of the initial transfer rate on acceptor concentration is observed in each of these ET pathways. The proportional coefficient as the averaged ET parameters for initial decay are determined, meaning the ET efficiency for the same concentration of acceptors follows the order of Pr³⁺–Pr³⁺ > Pr³⁺–Ce³⁺ > Ce³⁺–Pr³⁺–Pr³⁺. © 2010 American Institute of Physics.

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I. INTRODUCTION

Solid-state lighting based on white light-emitting diodes (LEDs) has attracted much interest in recent years due to its advantages of low applied voltage, long life, small size, and absence of mercury. At present, the main strategy for producing white light is combine blue LED with the yellow emitting Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce³⁺) phosphor, which can strongly absorb the blue light and subsequently emit yellow light, originating from the transition from the lowest 5d state to the ²F₅/₂ and ²F₇/₂ ground states of Ce³⁺.¹² However, YAG:Ce³⁺ has relatively weak emission in red spectral region, leading to low color rendering index for current white LEDs. To enhance the red component, Mueller-Mach et al.¹³ added Pr³⁺ into YAG:Ce³⁺ and consequently obtained additional sharp red line at about 608 nm, originating from ¹D₂ → ³H₂ transition of Pr³⁺, as only Ce³⁺ is excited by blue light at around 470 nm. The appearance of the red emission line of Pr³⁺ implies the performance of energy transfer (ET) from Ce³⁺ to Pr³⁺ in YAG:Ce³⁺, Pr³⁺. Subsequently, many studies on optical properties of YAG:Ce³⁺, Pr³⁺ were made.⁴⁻⁶ Further increasing Pr³⁺ concentration for obtaining enough red components to meet the requirement of white LEDs with high color rendering, however, the red line decreases due to self concentration quenching.⁵,⁶ In the present work, we observe that the red line can be continuously enhanced by increasing Ce³⁺ concentration as the quenching of the red line takes place. Besides Ce³⁺–Pr³⁺ ET, there also exists Pr³⁺–Ce³⁺ ET in YAG:Ce³⁺, Pr³⁺,⁶ reflecting a mutual ET system. Studies show that various ET processes play an important role on optical properties of YAG:Ce³⁺, Pr³⁺. To optimize the phosphor by controlling the concentrations of Ce³⁺ and Pr³⁺ in YAG, it is therefore significant to understand the dynamical processes of ET between the dopant ions, which to our knowledge have not been studied in detail. For Ce³⁺–Pr³⁺ ET, the main pathway is conformably 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 the ET takes place rather by non-radiative interaction, as suggested by Yang and Kim.⁶² In this case, Inokuti–Hirayama model is valid.

In this paper, we demonstrate various transfer pathways and transfer dynamical processes in Pr³⁺ and Ce³⁺ codoped YAG basing on the experimental measurements of photoluminescence (PL), photoluminescence excitation (PLE) spectra, and fluorescence decay curves. Moreover, the ET from Pr³⁺ to Ce³⁺ is also studied. The relative PL intensities of Ce³⁺ and Pr³⁺ as a function of Ce³⁺ and Pr³⁺ concentrations are analyzed, exhibiting a good agreement with the results evaluated from fluorescence decay data.
The powder samples have been prepared by conventional solid-state reaction. Y$_2$O$_3$, CeO$_2$, Al$_2$O$_3$, and Pr$_6$O$_{11}$ are mixed in a molar of \( (Y_{1-x-y}Ce_xPr_y)Al_3O_{12} \) \( (Y_{0.99}Ce_{0.01})Al_3O_{12} \) and \( (Y_{0.95}Pr_{0.05})Al_3O_{12} \) and \( (Y_{0.985}Ce_{0.01}Pr_{0.005})Al_3O_{12} \). A 3 wt% BaF$_2$ has been added to as the flux. After a good mixing in an agate mortar, the mixture has been sintered at 1500 °C for 3 h under a reducing atmosphere. The structure of the final products is characterized by power x-ray diffraction (XRD). The XRD patterns are in good agreement with Joint Committee for Powder Diffraction Standard file 33-0403Al$_5$O$_{12}$. The PL and PLE spectra monitoring at 605 nm and 611 nm within the broad emission band of Ce$^{3+}$ appear the strong UV PLE bands of Pr$^{3+}$ at 288 nm. This indicates a pronounced ET from Ce$^{3+}$ to Pr$^{3+}$. Moreover, it is also observed in Figs. 1d and 1e that the PLE spectra monitoring at 605 and 611 nm within the broad emission band of Ce$^{3+}$ appear the strong UV PLE bands of Pr$^{3+}$ at 288 nm. This indicates a pronounced ET from Ce$^{3+}$ to Pr$^{3+}$.

### II. EXPERIMENTAL

The powder samples have been prepared by conventional solid-state reaction. Y$_2$O$_3$, CeO$_2$, Al$_2$O$_3$, and Pr$_6$O$_{11}$ are mixed in a molar of \( (Y_{1-x-y}Ce_xPr_y)Al_3O_{12} \) \( (x, y \text{ represent the concentration of Ce}^{3+} \text{ and Pr}^{3+}, \text{ respectively}), 3 \text{ wt} % \text{ BaF}_2 \text{ has been added to as the flux. After a good mixing in an agate mortar, the mixture has been sintered at 1500 °C for 3 h under a reducing atmosphere. The structure of the final products is characterized by power x-ray diffraction (XRD). The XRD patterns are in good agreement with Joint Committee for Powder Diffraction Standard file 33-040. The PL and PLE spectra are measured at room temperature with a Hitachi Spextra-fluorometer (F-4500). The decay of the fluorescence from Ce$^{3+}$ is measured by an FL920 fluorimeter (Edinburgh Instruments, Livingston, U.K.) with a hydrogen flash lamp (nF900; Edinburgh Instruments). In the measurements of the fluorescent decay of Pr$^{3+}$, an optical parametric oscillator is used as an excitation source. The signal is detected by a Tektronix digital oscilloscope (TDS 3052).

### III. RESULTS AND DISCUSSION

#### A. Spectroscopic evidence of ET

Figure 1 shows the PL and PLE spectra of three samples, namely Ce$^{3+}$ singly doped \( (Y_{0.99}Ce_{0.01})Al_3O_{12} \) (a), Pr$^{3+}$ singly doped \( (Y_{0.99}Pr_{0.01})Al_3O_{12} \) (b), and Ce$^{3+}$, Pr$^{3+}$ doubly doped \( (Y_{0.985}Ce_{0.01}Pr_{0.005})Al_3O_{12} \) (c), respectively. The Ce$^{3+}$ singly doped sample exhibits a well known yellow emitting broad band due to the transition from the lowest-lying 5d state to the 4f ground state, peaking at around 530 nm. The PLE spectrum of the yellow band consists of a group of PLE bands, including a blue PLE band at 470 nm corresponding to the transition from the ground state to the lowest-lying 5d state, and two ultraviolet (UV) PLE bands corresponding to the upper 5d states, located at 340 nm and 230 nm, respectively, as shown in Fig. 1(a). The Pr$^{3+}$ singly doped sample exhibits three groups of emission of Pr$^{3+}$ upon 288 nm excitation, as shown in Fig. 1(b). The group in the UV region consists of two strong bands located at 317 nm and 381 nm, which are originated in the transitions from the lowest-lying 4f5d state to 3H$_{5/2}$ (J = 4, 5, 6) and 3F$_{2}$ (J = 2, 3, 4) states, respectively. The group in the range of 450–600 nm originates from the intense blue emission line at 488 nm due to the 3P$_0$ – 3H$_{4}$ transition. Another group in red originates from the intense red emission line at 608 nm with a weak satellite line at 640 nm. The PLE spectra of the three groups of emission in Pr$^{3+}$ singly doped sample are identical in the UV spectral range, showing two 4f5d PLE bands located at 288 nm and 238 nm, respectively. In Fig. 1(c), the PL spectrum of Ce$^{3+}$ and Pr$^{3+}$ doubly doped sample contains not only the yellow band of Ce$^{3+}$ but also the intense red lines of Pr$^{3+}$ when only Ce$^{3+}$ is excited at 340 nm, demonstrating occurrence of ET from Ce$^{3+}$ to Pr$^{3+}$. To further exam the ET in the doubly doped sample, the PLE spectrum of the pure 608 nm red line is obtained, as shown in Fig. 1(f), by subtracting the PLE spectrum monitoring the feet of the 608 nm lines from that in Fig. 1(c) monitoring the peak of the 608 nm lines. The PLE spectrum of the feet of the 608 nm line is obtained by averaging that monitoring 605 nm and 611 nm, as shown in Figs. 1(d) and 1(e), respectively. It is clearly presented that the PLE spectrum of the pure 608 nm emission line of Pr$^{3+}$, as shown in Fig. 1(f), contains the strong blue and the UV PLE bands of Ce$^{3+}$, which are absent in Pr$^{3+}$ singly doped sample. As a result, ET from Ce$^{3+}$ to Pr$^{3+}$ is evident.

Moreover, it is also observed in Figs. 1(d) and 1(e) that the PLE spectra monitoring at 605 and 611 nm within the broad emission band of Ce$^{3+}$ appear the strong UV PLE band of Pr$^{3+}$ at 288 nm. This indicates a pronounced ET from the lowest-lying 4f5d state of Pr$^{3+}$ to the 5d state of Ce$^{3+}$.

#### B. Ce$^{3+}$–Pr$^{3+}$ ET

Figure 2 shows the PL spectra of sample series A \( (Y_{0.99-x}Ce_{0.01}Pr_x)Al_3O_{12} \) with a fixed Ce$^{3+}$ concentration at 0.01 and various Pr$^{3+}$ concentration x in the range of 0–0.02. In order to avoid direct excitation into the 3P$_{2}$ (J = 0, 1, 2) levels of Pr$^{3+}$, we do not use 470 nm as an excitation to populate the lowest-lying 5d state of Ce$^{3+}$, instead we use 340 nm to excite the upper 5d state of Ce$^{3+}$. Besides a rapid relaxation down to the lowest 5d state, the excited upper 5d state of Ce$^{3+}$ may have additional two possible pathways for deexcitation, which are radiative transition to the ground state and ET to the 3P$_{2}$ states of Pr$^{3+}$. In our experiments, a weak purple emission band from the upper 5d state was indeed observed at about 380 nm. However, the 3P$_0$ – 3H$_{4}$ blue...
emission line of Pr$^{3+}$ was not detected at 488 nm for various x values. This behavior indicates that the pathway of Ce$^{3+}$–Pr$^{3+}$ ET hardly starts from both of the upper 5d state and the lowest 5d state of Ce$^{3+}$ to the $3P_0$ level of Pr$^{3+}$, as illustrated in Fig. 3. This conclusion is also supported by the fact that both the purple and yellow emission bands of Ce$^{3+}$ do not spectrally overlap with the $^3H_4$–$^3P_1$ absorption lines of Pr$^{3+}$ in the blue spectral region. The appearance of the red emission line of Pr$^{3+}$ for x > 0 is therefore, the result of ET from the lowest 5d of Ce$^{3+}$ to the $^1D_2$ of Pr$^{3+}$ because the yellow emission band of Ce$^{3+}$ has a spectral overlap with the red line (zero-phonon line) of Pr$^{3+}$. Basing on this ET pathway, we focus our study on the PL integrated intensity ratio of the red line from Pr$^{3+}$ as an acceptor to the yellow band from Ce$^{3+}$ as a donor because a large red/yellow ratio is significant for fabricating white LEDs with high color rendering index. In Fig. 2, where the intensity of the yellow band is normalized in each PL spectrum, it is observed that the red line grows up with increasing x until it reaches the maximum at x around 0.005. Subsequently, the red line falls down with further increasing x. The growth of the red line naturally implies the increase in the efficiency of Ce$^{3+}$–Pr$^{3+}$ ET. The decrease for x higher than 0.005 is attributed to concentration self-quenching by another Pr$^{3+}$ in the ground state through a cross relaxation, as described by $(^1D_2, ^3H_4) \rightarrow (^1G_4, ^3F_j)$.\color{brown}{11,12} The quenching has been proved by the observation of rapid shortening of the $^1D_2$ lifetime with increasing x, as described in Sec. III C. If the red/yellow ratio is governed by Ce$^{3+}$–Pr$^{3+}$ ET and self-quenching of Pr$^{3+}$, each value of the ratio relates to the corresponding fluorescence lifetimes of Ce$^{3+}$ and Pr$^{3+}$. In donor-acceptor ET system, due to nonexponential decay of donor fluorescence intensity $I_D(t)$ in the presence of acceptors, we define an average fluorescence lifetime of the donors as

$$\langle \tau_D \rangle = \int_0^\infty I_D(t) dt,$$

where $I_D(t)$ is normalized to its initial intensity. The luminescence efficiency of the donors is given by $\eta_D = \eta_A \tau_A / \tau_D$ with $\tau_D$ being the intrinsic lifetime of the donor fluorescence. In the absence of acceptors, the $\langle \tau_D \rangle$ especially labeled by $\langle \tau_D \rangle_0$ is equal to $\tau_D$, if the donor concentration is sufficient low, otherwise $\langle \tau_D \rangle$ may be less than $\tau_D$ due to various nonradiative quenching processes induced by donors. If $\langle \tau_D \rangle_0^{-1} - \langle \tau_D \rangle_0^{-1} \ll \tau_D^{-1}$, i.e., the donor induced quenching rate much less than the radiative rate, the fluorescence still keeps an exponential decay in the time scale of $\tau_D$. In this case, the efficiency of donor-acceptor ET is then written as $\eta_D = 1 - (\langle \tau_D \rangle - \langle \tau_D \rangle_0) / \langle \tau_D \rangle_0$. The luminescence efficiency of acceptors is given by $\eta_A = \tau_A / \tau_D$ with $\langle \tau_A \rangle$ and $\tau_A$ being the average and intrinsic fluorescence lifetimes for the acceptors, respectively. In continuous excitation of donors, the PL intensity ratio of the acceptors to the donors is then expressed by

$$I_A / I_D = \eta_A / \eta_D = \left( \frac{1}{\langle \tau_A \rangle} - \frac{1}{\langle \tau_D \rangle_0} \right) \frac{\tau_D}{\tau_D},$$

where the term $(1/\langle \tau_A \rangle - 1/\langle \tau_D \rangle_0)$ is the macroscopic ET rate. Equation (2) indicates that in ET system the PL intensity ratio changes synchronously with the value of $(1/\langle \tau_A \rangle - 1/\langle \tau_D \rangle_0)$, which can be calculated using the measured values of the average lifetimes of the donor and the acceptor fluorescence. To test the validity of Eq. (2) in YAG:Ce$^{3+}$, Pr$^{3+}$, we have measured the decay curves of the yellow fluorescence of Ce$^{3+}$ and the red fluorescence of Pr$^{3+}$ for different x in sample series A, as shown in Figs. 4 and 5, respectively. The decay of the yellow fluorescence is measured by monitoring at 530 nm upon 340 nm pulsed excitation and that of the red fluorescence by monitoring $^1D_2 \rightarrow ^3H_4$ emission of Pr$^{3+}$ at 714 nm upon $^3H_4 \rightarrow ^1D_2$ pulsed excitation at 608 nm. The average lifetimes obtained from these decay patterns are listed in Table I. It is found that the decay of the red fluorescence speeds up rapidly with increasing x, indicating a strong self-quenching. Labeling the emitting state of the donor Ce$^{3+}$ by 1 and that of the acceptor Pr$^{3+}$ by 2, the x dependence of the red/yellow ratio $(I_2/I_1)$ obtained from PL spectra and that calculated using $(1/\langle \tau_2 \rangle - 1/\langle \tau_1 \rangle) / \langle \tau_2 \rangle$ are both plotted in Fig. 6, clearly demonstrating their identical x.

**Fig. 2.** (Color online) PL spectra of $(Y_{0.99-x}Ce_{0.01}Pr_x)Al_2O_12$ (x = 0–0.02) under 340 nm excitation. The intensity of the yellow band in each spectrum is normalized.

**Fig. 3.** (Color online) Energy level diagrams of Ce$^{3+}$ and Pr$^{3+}$ with the indicated pathway of Ce$^{3+}$–Pr$^{3+}$ ET.
must analyze the absolute intensity of the red line that is at \( x \) below 0.005 because the value of quenching strongly limits the maximal absolute PL intensities is an important parameter for optimizing the x dependence of the 1D2 level through the cross relaxation as mentioned above. If the strongest red line is required instead of the red/yellow ratio, we must analyze the absolute intensity of the red line that is written as \( \eta_{DA} \eta_{A} \). Comparing to the red/yellow ratio expressed as \( \eta_{DA} \eta_{A} / \eta_{D} \), the maximum of \( \eta_{DA} \eta_{A} \) should occur at \( x \) below 0.005 because the value of \( \eta_{D} \) reduces with increasing \( x \). For \( x < 0.005 \), the loss of the overall PL intensity is estimated to be less than 0.1 using the lifetimes listed in Table I. The self-quenching strongly limits the maximal value of the red/yellow ratio and the absolute intensity of the red line. Fortunately, the enhancement of this ratio has been performed by increasing Ce\(^{3+} \) concentration, which will be demonstrated in Sec. III D.

The decays in Figs. 4 and 5 change from exponential to nonexponential patterns with increasing \( x \), reflecting the effect of ET. The normalized intensity of the donor fluorescence can be written as

\[
I_D(t) = I_{D0}(t)f(t),
\]

where \( I_{D0}(t) \) is the decay function of donors in the absence of acceptors, the function \( f(t) \) characterizes the loss of excited donors due to one way ET to the acceptors. If ET rate between a donor and an acceptor is proportional to an inverse power of the distance \( r \), writing as \( \alpha / r^m \), according to Inokuti–Hirayama formula, we have

\[
f(t) = \exp \left[ -\frac{4}{3} \pi \frac{1}{m} \frac{3}{m} \left( \frac{3}{m} \right) \right],
\]

where \( \alpha \) is a rate constant for ET, \( m = 6,8,10 \), the coefficient for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interaction, respectively. \( n_A \) is the number of acceptor ions per unit volume. From Eqs. (3) and (4), \( \log[\ln[I_D(t)/I_{D0}(t)] \) acts as a linear function of \( \log(t) \) with a slope of \( 3/m \), and \( \ln[I_D(t)/I_{D0}(t)] \) is proportional to \( t^{3/m} \) with

<table>
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<th>( x )</th>
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<th>( \lambda_{cm} ) (nm)</th>
<th>( \eta_x )</th>
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<tr>
<td>0.02</td>
<td>30.3</td>
<td>20</td>
<td>0.48</td>
</tr>
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</table>

FIG. 4. (Color online) Decay curves of the yellow fluorescence in \( \text{Y}_{0.99-x}\text{Ce}_{0.01}\text{Pr}_x\text{Al}_2\text{O}_12 \) for \( x = 0, 0.005, 0.01, \) and 0.02.

FIG. 5. (Color online) Decay curves of the red fluorescence intensity for \( x = 0, 0.005, 0.01, \) and 0.02.

FIG. 6. (Color online) \( x \) dependence of ratio \( I_2/I_1 \) obtained directly from PL spectra with that evaluated using \( (1/\tau_x - 1/\tau_y) / \tau_y \) for samples \( \text{Y}_{0.99-x}\text{Ce}_{0.01}\text{Pr}_x\text{Al}_2\text{O}_12 \) (\( x = 0 - 0.02 \)). The maximal value of the ratio is normalized.
a slope of $-4\pi(1-3/m)n_A\alpha^{3/m}/3$. Figure 7(a) shows the log-log plot of $\ln[I_{10}(t)/I_{10}(0)]$ versus $t$ for sample $(Y_{0.99-x}Ce_{0.01}Pr)_3Al_5O_{12}$ with $x=0.02$ (a) and plotted $\ln[I(t)/I_{10}(t)]$ versus $t^{1/2}$ for the samples $(Y_{0.99-x}Ce_{0.01}Pr)_3Al_5O_{12}$ with $x=0.01$ and 0.02 (b). The solid lines indicate the fitting behaviors.

![FIG. 7. (Color online) log-log plot of $\ln[I_{10}(t)/I_{10}(0)]$ vs $t$ for sample $(Y_{0.99-x}Ce_{0.01}Pr)_3Al_5O_{12}$ with $x=0.02$ (a) and plotted $\ln[I(t)/I_{10}(t)]$ vs $t^{1/2}$ for the samples $(Y_{0.99-x}Ce_{0.01}Pr)_3Al_5O_{12}$ with $x=0.01$ and 0.02 (b). The solid lines indicate the fitting behaviors.](Image)

Using the value of $\alpha$, the critical ET distance $r_0$ (the spatial separation between a donor and an acceptor where the ET rate $\alpha/\alpha^0=1/\tau_{00}$) is calculated to be about 0.81 nm. In the calculation, the intrinsic lifetime $\tau_{10}$ is 61 ns determined in 0.0005 Ce$^{3+}$ lowly doped YAG, which exhibits a pure exponential decay.

In Fig. 7(a) there is an increase in slope below 20 ns, forming a crossover. As we know, Eq. (4) is obtained by assuming the nearest distance between a donor and an acceptor to be 0, leading to an infinite initial ET rate. Hence, Eq. (4) is not applicable at short times which is less than 20 ns in the present sample. In the case of discrete lattices, the initial ET rate is described by

$$W_{DAi} = x \sum_l w_{0i}.$$  

(5)

where $w_{0i}$ is the ET rate from a donor at site 0 to an acceptor at site $l$ excluding $l=0$. The function $f(t)$, therefore, exhibits a linear behavior $f(t) \sim \exp[-W_{DAi}]$ at short times and a $t^{3/m}$ variation at longer times. In random distribution of acceptors in host lattices $\Sigma w_{0i}$ is the averaged ET parameter, denoting the total ET rate of a donor ion embedded within a complete acceptor environment ($x=1$). In the present work, the sample for $x=0$ shows an exponential decay of fluorescence. Therefore, $\Sigma w_{0i}$ can be experimentally obtained by using the following linear relationship with the initial decay rate $W_{Di}$ of the donor fluorescence

$$W_{Di} = x \sum_l w_{0i} + \langle \tau_D \rangle^{-1}.$$  

(6)

Figure 8 shows a linear dependence of $W_{11}$ on $x$ in sample series A $(Y_{0.99-x}Ce_{0.01}Pr)_3Al_5O_{12}$ ($x=0–0.02$). The slope gives the value of $\Sigma w_{0i}$ to be around 1.2 ns$^{-1}$, yielding $\tau_{10} \Sigma w_{0i}$ to be 73, where $\tau_{10}=61$ ns.

C. Pr$^{3+}$–Pr$^{3+}$ ET

The decay patterns of Pr$^{3+}$ $^1D_2$ are analyzed in sample series A to understand the self-quenching through a cross relaxation, as described by $^1D_2,^3H_4) - (^1G_4,^3F_4)$. The log-log plot of $\ln[I_{20}(t)/I_{20}(t)]$ versus $t$ for sample $(Y_{0.99-x}Ce_{0.01}Pr)_3Al_5O_{12}$ with $x=0.02$ is shown in Fig. 9(a). The $I_{20}(t)$ is an pure exponential decay function exp(−$t/\tau_{20}$) with $\tau_{20}=202$ ms being the intrinsic lifetime of the $^1D_2$ level of Pr$^{3+}$ in YAG obtained from the tail decay of the fluorescence in 0.001 Pr$^{3+}$ doped YAG. The slope for $t > 10$ ms is more close to 0.5, indicating an electric dipole-dipole ET between Pr$^{3+}$ ions. The linear dependence of $\ln[I_{20}(t)/I_{20}(t)]$ versus $t^{1/2}$ are observed and a good agreement between the theoretical and experimental results are performed for various $x$ when fixing the rate constant $\alpha$ to be $2.4 \times 10^{-38}$ cm$^6$ s$^{-1}$ for Pr$^{3+}$–Pr$^{3+}$ self-quenching, as shown in Fig. 9(b). The critical quenching distance of 1.3 nm is evaluated. Meanwhile, the linear dependence of the initial
decay rate of the red fluorescence \( W_{2i} \) on \( x \), as shown in Fig. 10, gives the value of \( \sum w_{2i} \) to be 6.2 \( \mu s^{-1} \), yielding \( \tau_{20} \sum w_{2i} \) to be 1252, which is a order of magnitude larger than 73 for Ce\(^{3+} \)–Pr\(^{3+} \) ET. This indicates that the self-quenching of Pr\(^{3+} \) \( 1D_2 \) by another Pr\(^{3+} \) in the ground state is more efficient than the Ce\(^{3+} \) \( 5d \)–Pr\(^{3+} \) \( 1D_2 \) ET.

FIG. 10. (Color online) Dependence of \( W_{2i} \) on \( x \) in \((Y_{0.99-x}Ce_{0.01}Pr_x)_{3}Al_5O_{12} \) (\( x = 0−0.02 \))

D. Ce\(^{3+} \)–Pr\(^{3+} \) ET versus Ce\(^{3+} \) concentration

In this section, we demonstrate the study on enhancing the red/yellow ratio by increasing Ce\(^{3+} \) concentration instead of Pr\(^{3+} \) to avoid concentration quenching. Figure 11 shows the PL spectra of sample series B \((Y_{0.995−y}Ce_{0.005}Pr_{0.005})_{3}Al_5O_{12} \) with Pr\(^{3+} \) concentration fixing at 0.005 and various Ce\(^{3+} \) concentration \( y \) in the range of 0–0.02. When the intensity of the yellow emission band of Ce\(^{3+} \) is normalized, it is found that the red emission line of Ce\(^{3+} \) monotonously grows up with increasing \( y \). As \( y = 0.02 \), the ratio is higher than that for \( x = 0.01 \), i.e., higher than the maximal ratio in sample series A demonstrated in section B. In view of small changes in the red fluorescence lifetimes with increasing \( y \) (see Table II), the enhanced red line is the indication of increased macroscopic Ce\(^{3+} \)–Pr\(^{3+} \) ET rate according to Eq. (2). One can find the existence in connection with the enhancement of the red/yellow ratio is a redshift in the yellow PL band with increasing \( y \). As \( y = 0.02 \), the ratio is higher than that for \( x = 0.01 \), i.e., higher than the maximal ratio in sample series A demonstrated in section B. In view of small changes in the red fluorescence lifetimes with increasing \( y \) (see Table II), the enhanced red line is the indication of increased macroscopic Ce\(^{3+} \)–Pr\(^{3+} \) ET rate according to Eq. (2). One can find the existence in connection with the enhancement of the red/yellow ratio is a redshift in the yellow PL band with increasing Ce\(^{3+} \) concentration, as has been observed in Ce\(^{3+} \) singly doped YAG. The redshift enhances the spectral distribution of the yellow band at the position of the red line, which does not shift with \( y \). As a result, we consider that the redshift is favorable for effectively increasing the spectral overlap integrals between the yellow emission band and the red absorption line, and therefore enhancing the ET rate which is proportional to the spectral overlap integrals between donor emission and acceptor absorption. Due to weak electron-phonon coupling in 4f configuration of rare earth ions, the position of the red emission line can be regarded as that of the zero-phonon absorption line. In the case of much narrower red line than the yellow band, their spectral overlap integral is proportional to the spectral intensity of the normalized yellow band at the red line site, \( I_{1R} \). As we plot the red/yellow ratio \( I_{2}/I_{1} \) versus \( I_{1R}(T) \), they approximately satisfy a proportional relationship, as shown in Fig. 12. Due to low Pr\(^{3+} \) concentration in sample series B, the reduction in the yellow fluorescent lifetimes is less than a half of the intrinsic lifetime even for the Ce\(^{3+} \) concentration as high as 0.02. Hence, the fluorescent decays are all approximately

FIG. 11. (Color online) PL spectra of \((Y_{0.995−y}Ce_{0.005}Pr_{0.005})_{3}Al_5O_{12} \) (\( y = 0−0.02 \)) upon 340 nm excitation, where the intensity of the yellow band in each spectrum is normalized.

FIG. 9. (Color online) log-log plot of \( \ln[I_{2}(t)/I_{20}(t)] \) vs \( t \) for sample \((Y_{0.99−x}Ce_{0.01}Pr_{0.01})_{3}Al_5O_{12} \) with \( x = 0.02 \) (a) and plotted \( \ln[I_{2}(t)/I_{20}(t)] \) vs \( 1/t \) for the samples \((Y_{0.99−x}Ce_{0.01}Pr_{0.01})_{3}Al_5O_{12} \) with various \( x \) (\( x = 0−0.02 \)) (b). The solid lines indicate the fitting behaviors.
exponential in the time scale of the intrinsic lifetime. It means the initial ET rate governs the macroscopic ET rate in sample series B. As we know the initial ET rate is proportional to the spectral overlap integrals between donor and acceptors, the proportional relationship in Fig. 12 is thus expected.

Another possibility causing the enhanced macroscopic ET rate is related to enhanced donor (Ce\(^{3+}\))-donor (Ce\(^{3+}\)) energy diffusion as increasing donor concentration.\(^{19}\) As we know, the diffusion does not change the initial decay rate of ET.\(^{20}\) We observe that the initial decay rate of the yellow fluorescence increases as increasing y with a slope of 0.30 ns\(^{−1}\) for y in the present range of 0–0.02, as shown in Fig. 13. While, the initial decay rate of fluorescence in Ce\(^{3+}\) singly doped YAG also increases with increasing y, but with a smaller slope, 0.17 ns\(^{−1}\). The enhanced decay in Ce\(^{3+}\) singly doped YAG can be resulted from some quenching centers generated by doping Ce\(^{3+}\) and the one way ET from the high energy Ce\(^{3+}\) ions to the low energy Ce\(^{3+}\) ions within the inhomogeneously broadened PL spectra for high Ce\(^{3+}\) concentration.\(^{21,22}\) If these ET processes are independent on Pr\(^{3+}\) concentration, the difference (0.13 ns\(^{−1}\)) between the two slopes reflects the increment of Ce\(^{3+}\)–Pr\(^{3+}\) ET rate due to the increase in the spectral overlap resulted from the red-shift in the yellow band with increasing y. The red/yellow ratio evaluated for various y by using Eq. (2) in relation to the macroscopic ET rates is roughly close to that from PL, as shown in Fig. 12. Using the initial ET rates \(W_{12}\) instead of the macroscopic ET rates, the evaluated red/yellow ratio by \(W_{12}/(\tau_{12})\) dose not change much due to the dominance of the initial ET in the whole ET in the Sample series B. Here, the initial ET rate is calculated using Eq. (6) with the data shown in Fig. 13. The absolute PL intensity reaches the maximum when Ce\(^{3+}\) concentration y is about 0.02. In this case, we experimentally found that the optimal concentration of Pr\(^{3+}\) occurs at 0.002, which limits the loss of the overall PL intensity less than 0.05 for practical use of the white LED phosphor.

### E. Pr\(^{3+}\)–Ce\(^{3+}\) ET

Figure 14 shows the PL spectra of sample series B (Y\(_{0.995−y}\)Ce\(_{0.005}\)Pr\(_{0.005}\))\(\alpha\)O\(_{12}\) (y = 0–0.02) as the lowest 4f5d state of Pr\(^{3+}\) is excited at 288 nm, where the UV PL band of Pr\(^{3+}\) is normalized. One can find the yellow PL band of Ce\(^{3+}\) increases with increasing y, exhibiting the enhanced efficiency of ET from Pr\(^{3+}\) to Ce\(^{3+}\). Considering that the lowest 4f5d PL bands of Pr\(^{3+}\) overlap well with the UV PLE band of Ce\(^{3+}\) in the range of 300–400 nm (see Fig. 1), the Pr\(^{3+}\)–Ce\(^{3+}\) ET may go from the lowest 4f5d state (labeled by

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**TABLE II.** Fluorescent lifetimes and transfer efficiencies in (Y\(_{0.995−y}\)Ce\(_{0.005}\)Pr\(_{0.005}\))\(\alpha\)O\(_{12}\).

<table>
<thead>
<tr>
<th>Y</th>
<th>(Pr^{3+}) 4f5d, (\tau_{2f} = 14) ns, ((\tau_{1f}) (\mu s))</th>
<th>(Pr^{3+}) f i r s t  (\tau_{2f} = 14) ns, ((\tau_{1f}) (\mu s))</th>
<th>(Ce^{3+}) 5d, (\tau_{2f} = 202) μs, ((\tau_{1f}) (\mu s))</th>
<th>(Ce^{3+}) 5d, (\tau_{2f} = 61) ns, ((\tau_{1f}) (\mu s))</th>
<th>(Ce^{3+}) 5d, YAG:γCe(^{3+}), ((\tau_{1f}) (\mu s))</th>
<th>(\eta_2)</th>
<th>(\eta_{41})</th>
<th>(\eta_{41})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14</td>
<td>8.8</td>
<td>162</td>
<td>53.3</td>
<td>61.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.001</td>
<td>11.2</td>
<td>7.7</td>
<td>85</td>
<td>50.7</td>
<td>60.1</td>
<td>0.12</td>
<td>0.20</td>
<td>0.13</td>
</tr>
<tr>
<td>0.003</td>
<td>9.9</td>
<td>6.8</td>
<td>72</td>
<td>51.1</td>
<td>59.3</td>
<td>0.16</td>
<td>0.30</td>
<td>0.23</td>
</tr>
<tr>
<td>0.005</td>
<td>7.9</td>
<td>6.5</td>
<td>82</td>
<td>48.7</td>
<td>58.4</td>
<td>0.14</td>
<td>0.44</td>
<td>0.26</td>
</tr>
<tr>
<td>0.007</td>
<td>6.3</td>
<td>5.9</td>
<td>85</td>
<td>46.0</td>
<td>57.2</td>
<td>0.17</td>
<td>0.55</td>
<td>0.33</td>
</tr>
<tr>
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<td>5.4</td>
<td>90</td>
<td>43.5</td>
<td>53.5</td>
<td>0.20</td>
<td>...</td>
<td>0.39</td>
</tr>
<tr>
<td>0.02</td>
<td>...</td>
<td>4.1</td>
<td>90</td>
<td>41.0</td>
<td>53.5</td>
<td>0.19</td>
<td>...</td>
<td>0.53</td>
</tr>
</tbody>
</table>
4) of Pr$^{3+}$ to the 5$d$ states of Ce$^{3+}$, as illustrated in Fig. 15. Another possible transfer pathway from Pr$^{3+}$ 3$P_0$ (labeled by 3) to the lowest 5$d$ state of Ce$^{3+}$ is also indicated. The 3$P_0$–5$d$ transfer has lead to intensity reduction of the 3$P_0$–3$H_4$ emission line at 488 nm followed by lifetime shortening of the 3$P_0$ level as $y$ is increased. We observed experimentally that the decay for $y=0$ is purely exponential with a lifetime $\langle \tau_3 \rangle_0$ of about 8.8 $\mu$s. Ozen et al.\textsuperscript{19} has measured the decay of 3$P_0$ level in YAG:Pr$^{3+}$ at 20 k and obtained the intrinsic lifetime to be 14 $\mu$s. They proved that the shortening of the lifetime at room temperature is due to enhanced multiphonon relaxation to the lower state 1$D_2$ and therefore this process does not change its exponential decay behavior. It should be noted that the lifetime of the 1$P_0$ decreases from 8.8 to 4.1 $\mu$s, only reducing a half of the $\langle \tau_3 \rangle_0$ with increasing $y$ up to 0.02, as listed in Table II. However, the intensity of the blue PL line reduces faster than its lifetime and almost disappears at $y=0.02$. We have experimentally proved that this behavior is due to reabsorption of the blue PL by the lowest 5$d$ state of Ce$^{3+}$. As the 4f5$d$ of Pr$^{3+}$ is excited, besides the ET to the 5$d$ state of Ce$^{3+}$, part of the excitation energy may relax directly down to the 3$P_0$, which subsequently relaxes down to the lower level 1$D_2$. It is found in Fig. 14 that the totally integrated PL intensities of the whole emission lines from 3$P_0$ and 1$D_2$ are much less than that from the 4f5$d$ band for $y=0$. It implies that only a small part of the 4f5$d$ relaxes down to the lower levels. This conclusion is also supported by the result obtained by Weber\textsuperscript{23} that the fluorescent quantum efficiency of the lowest 4f5$d$ state is near to unity due to a large energy gap $\sim 10,000$ cm$^{-1}$ between the lowest 4f5$d$ and the nearest 1$P_0$ manifold of the 4f configuration. Moreover, for each $y$ the 1$P_0$ 5$d$ ET efficiency $\eta_{31}$ is less than the 4f5$d$–5$d$ ET efficiency $\eta_{11}$, as listed in Table II. Therefore, the ET from the 1$P_0$ of Pr$^{3+}$ to the 5$d$ of Ce$^{3+}$ can be neglected in comparison with the transfer from the 4f5$d$ of Pr$^{3+}$ to the 5$d$ of Ce$^{3+}$.

The Pr$^{3+}$–Ce$^{3+}$ ET leads to the reduction of the UV fluorescence intensity and lifetime with the increase in $y$. Figure 16 shows the decay curves of the UV fluorescence of Pr in (Y$_0.995$Ce$_y$Pr$_{0.005}$)Al$_5$O$_{12}$ for $y=0$, 0.003, and 0.007.
Ce$^{3+}$. This value is larger than 73 for Ce$^{3+}$ – Pr$^{3+}$ ET but smaller than 1252 for Pr$^{3+}$ – Pr$^{3+}$ ET.

Also shown.

$0.005$ Pr$^{3+}$ are measured as the $4f$ population of $^{1}D_{2}$ may possibly be provided through the following three ways, the direct feed by the $4f$ of Pr$^{3+}$ to the $5d$ state of Ce$^{3+}$. A strong dipole–dipole interaction. For Ce$^{3+}$ concentration of 0.01, the corresponding rate constant and critical distance are evaluated to be $4.5 \times 10^{-36}$ cm$^5$ s$^{-1}$, 0.81 nm for Ce$^{3+}$–Pr$^{3+}$ ET and $2.4 \times 10^{-38}$ cm$^5$ s$^{-1}$, 1.30 nm for Pr$^{3+}$–Pr$^{3+}$ ET. Spectroscopic study also demonstrates a pronounced ET from the lowest $4f$d of Pr$^{3+}$ to the $5d$ of Ce$^{3+}$.

A proportional dependence of the initial transfer rate on acceptor concentration is observed in each of these ET pathways. The proportional coefficient as the averaged ET parameters for initial decay are determined to be $73 \tau_{0}$ for ET from Ce$^{3+}$ lowest $5d$ to Pr$^{3+}$ $^{1}D_{2}$, 1252 $\tau_{0}$ for ET from Pr$^{3+}$ $^{1}D_{2}$ to another Pr$^{3+}$ in the ground state, and $237 \tau_{0}$ for ET from Pr$^{3+}$ lowest $4f$d to Ce$^{3+}$ $5d$ states, respectively, meaning the ET efficiency for the same concentration of acceptors follows the order of Pr$^{3+}$–Pr$^{3+}$ > Pr$^{3+}$–Ce$^{3+}$ > Ce$^{3+}$–Pr$^{3+}$.

The relative PL intensities of Ce$^{3+}$ and Pr$^{3+}$ for various Ce$^{3+}$ and Pr$^{3+}$ concentrations are in good agreement with the results evaluated from fluorescence decay data.

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