Measurement of quantum efficiency in Pr$^{3+}$-doped CaAl$_4$O$_7$ and SrAl$_4$O$_7$ crystals

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We demonstrated a method for measuring the quantum efficiency of deep UV emission using the two-step excitation and the difference of the integrated spectral intensities in Pr$^{3+}$-doped CaAl$_4$O$_7$ and SrAl$_4$O$_7$ crystals. The quantum efficiencies of the emission from the lowest 4$f_5d$ state in the two systems have been estimated to be less than 10% at room temperature. The effect of excited-state absorption of the lowest 4$f_5d$ state is analyzed for the quantum efficiency measurement. The actual efficiency may be higher when this effect is taken into account, especially under the condition of strong excitation. © 2001 American Institute of Physics. [DOI: 10.1063/1.1407296]

Trivalent praseodymium (Pr$^{3+}$) ions, as active fluorescent centers, have been studied in a variety of hosts. 1–4 There are two possible arrangements for the positions of 1$S_0$ state and the 4$f_5d$ band. In the first arrangement, the lowest 4$f_5d$ state lies above the 1$S_0$ state of the 4$f^2$ configuration. This is the situation in some fluorides, some aluminates, and borates with Pr$^{3+}$ ions at the high coordination sites. Parity-allowed excitation to the 4$f_5d$ band will quickly relax to the 1$S_0$ state where the electrons further relax and yield optical emissions. The quantum efficiency (QE) of 1$S_0$ can be higher than 100%, as shown in YF$_3$:Pr$^{3+}$. The second case is Pr$^{3+}$ in YAG, LiYF$_4$, and the crystals presented in the letter, where the lowest 4$f_5d$ state lies below the 1$S_0$ state, excitation to the 4$f_5d$ band will relax to the lowest state in the band, yielding the emission in the broad spectral range. For emission from either the 1$S_0$ state or the lowest band, deep UV excitation is required.

The determination of QE using one-photon excitation, especially for solid samples, has been shown to be very difficult and controversial for the results. 5–7 It is even more difficult for our small fiber samples with a deep UV source. The purpose of this work is to demonstrate a method for measuring the emission efficiency without using a deep UV source in Pr$^{3+}$:CaAl$_4$O$_7$ (CAO:Pr) and Pr$^{3+}$:SrAl$_4$O$_7$ (SAO:Pr) systems. The method uses two-photon stepwise excitation to pump the electrons from the ground state to the 4$f_5d$ band. The emission spectra can be detected in both the UV and visible ranges. Optical transitions are identified and the quantum efficiency determined using the difference of the spectral intensities obtained from different pumping mechanisms. The QEs measured for the lowest 4$f_5d$ band in both samples are less than 10%. An influence in the QE measurements due to the excited-state absorption (ESA) is discussed. The actual QEs may be higher when the ESA effect is taken into account.

CAO:Pr and SAO:Pr single-crystal fibers were prepared using the laser-heated pedestal growth method. 8 The concentrations of Pr$^{3+}$ are 5 at. % for CAO:Pr and 1 at. % for SAO:Pr. The trivalent rare-earth ions replace divalent Ca or Sr ions in the host. 5 and 1 at. %, Mg was codoped into each sample, respectively, substituting for Al ions for charge compensation purposes. The fluorescence measurements were taken using either a SPEX FluroMax spectrofluorimeter or an EG&G charge-coupled-device (CCD) spectograph. A Spectra Physics/Quanta Ray Nd:YAG pumped LAS LDL 20505 dye laser system was used as a pulsed excitation source. The fluorescence decay was recorded using a Tektronix 460 A digital oscilloscope and a SPEX M500 spectrometer.

A schematic diagram of the experimental setup for efficiency measurements is shown in Fig. 1. Frequency-tripled YAG laser output (355 nm, 5 ns) is used to pump a three-stage dye (Coumarin 480) laser. The dye laser is tuned at 463 nm to populate the $^3P_1$ state, from which the electrons will quickly relax to $^3P_0$ and yield strong red emissions ($^3P_0$ – $^3F_{2,3,4}$). A small portion of the 355 nm UV output from the YAG laser is separated and optically delayed for 15 ns following the end of the dye laser pulse at the sample. The delayed UV pulses will further excite the electrons from the $^3P_0$ state to the 4$f_5d$ band. This will give strong UV emis-

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visions (4f5d−3Hj,3Fj) and reduce the emission intensity from the 3P0 state. The emission is collected into an optic fiber cable and sent to a CCD spectrograph. Assuming the number of electrons excited from the 3P0 to the 4f5d band and then relaxed to the lowest state of the band is Δn0 and the QE of the state is η1, the number of photons emitted from the state will be η1Δn0. If the QE of the 3P0 state is η0 and branch ratios of 4f5d−3H4,5,6, 3F2,3,4, 4f5d−3P0/1I6, and 3P0−3F2 transitions are β1, β1', and β0, respectively, the emission intensity of 4f5d−3H4,5,6, 3F2,3,4,I1, and the decrease of 3P0−3F2 emission due to the UV pump, ΔI0, can be expressed as follows:

\[ I_1 = η_1 Δn_0, \]
\[ ΔI_0 = η_0 Δn_0 (1 − β_1 η_1). \]

Let \( R = I_1 / ΔI_0 \), we find the QE of the band,

\[ η_1 = R β_0 η_0 (β_1 + R β_0 β_1 η_0). \]  

All the information on the right side of Eq. (3) can be obtained from the spectral measurements. Detailed calculations will be presented in the next section, followed by a discussion of the ESA effect of the lowest 4f5d state on the QE measurements.

Figure 2 shows the excitation (monitored at 276 nm) and emission (excitation at 225 nm) spectra of SAO:Pr involved in the 4f5d band. The broad features for both excitation and emission are clearly observed. For the emission spectrum, visible emissions are not detected; all of the emissions occur in the UV region. This is consistent with a theoretical calculation showing that the major components of the lowest 4f5d band mixture are the 4f5d3Hj and 4f5d3Fj manifolds. Hence, only the transitions to the 4f23Hj and 4f23Fj states are allowed. By deconvoluting the emission spectrum, we can identify the 4f5d emissions to different transitions, as indicated in Fig. 2.

Figure 3 represents the emission spectra (intensity corrected) of Pr:SAO (a) and Pr:CAO (b) used for the QE calculation. Line I0 is the spectrum of the 3P0−3F2 transition under 463 nm excitation. I0' is the spectrum of the 3P0−3F2 transition under both 463 and 355 nm excitations, and ΔI0 the difference of I0 and I0'. The inset shows the up-converted UV emission from the lowest 4f5d state under stepwise excitation of 463 and 355 nm when I0' is recorded. The ratio R can be obtained from the integrated spectra. η0 can be estimated in the range of 0.7−1.0. The transitions from the lowest 4f5d state to 3P0 or 1I6 are forbidden, nearly all the electrons from the 4f5d state relax to the 3H4,5,6 and 3F2,3,4 states, i.e., β1' ≈ 0 and β1 ≈ 1. β0 can be obtained from the emission spectra with a value of 0.21. QEs are then calculated to be 6.3%−9.0% and 4.2%−6.0% for SAO:Pr and CAO:Pr, respectively.

All the QEs obtained are less than 10%. There are two factors accounting for the low QEs. First, the trap/defect centers may interact with the lowest 4f5d state in the crystal, causing strong nonradiative relaxation of the state and, therefore, reducing the quantum efficiency. The measured QEs truly reflect the properties of the 4f5d state. Second, the low QE may be affected by the ESA of the lowest 4f5d state, resulting in some electrons in the lowest 4f5d state moving to the conduction band and then releasing their energy to some trap centers of the host crystals. The values of the measured QE may be manipulated by the effect. In the following, we will discuss the ESA influence in the QE measurement.

The expression in Eq. (3) is obtained without considering the ESA of the lowest 4f5d state. However, the cross section of the ESA reported for the lowest 4f5d state is greater than that of the 3P0 state in some crystals doped with Pr3+ ions. Equation (3) may need some modification if strong UV excitation causes ESA of the lowest 4f5d state. In this case, ESA will send electrons to the conduction band, where they are captured by some trap centers. In general, the rate of the electrons being captured is high, while the rate of the electrons being released from the traps is low in comparison to the lifetime of the lowest 4f5d state.

Assume the laser pulse is rectangular with photon flux density F and duration tP and the electronic populations in 3P0, the lowest 4f5d state, and the conduction band are n0, n1, and n2, respectively, we can readily obtain n0 and n1 from the rate equations during the pulse,

\[ n_0 = N_0 e^{-F t_P}, \]
\[ n_1 = F \sigma_0 N_0 \frac{F_{\sigma_1}}{F_{\sigma_1} + F_{\sigma_1'} - e^{-F t_P'}}, \]

where \( F_{\sigma_0} = F \sigma_0 + \gamma_0 \) and \( F_{\sigma_1} = F \sigma_1 + \gamma_1 \), \( \sigma_0 \) and \( \sigma_1 \) are the absorption cross sections of 3P0 and the lowest 4f5d state, respectively, and \( \gamma_0 \) and \( \gamma_1 \) are the decay rates of the 3P0.
and the lowest $4f5d$ states, respectively. $N_0 = n_0(t=0)$, where the zero time is set when the UV pulse arrives at the sample. $N_0$ is nearly constant during the UV excitation since $t_p$ is much smaller than the lifetime of the $3P_0$ state. After $t = t_p$, $n_0$ and $n_1$ decay with rate $\gamma_0$ and $\gamma_1$, respectively. Since $t_p$ (5 ns) $\ll 1/\gamma_1 (15 \mu s)$, the integrated intensity of the $3P_0$ emission, $I'_0$, must include the contribution during the pulse and can be expressed as follows:

$$I'_0 = \eta_0 \int_0^{t_p} e^{-\gamma_0 t} dt + \int_0^{t_p} e^{-\gamma_0 (t-t_p)} dt$$

$$= \eta_0 N_0 \left[ \gamma_0 + F \sigma_0 e^{-F \omega_p} \right]. \quad (5)$$

Similarly, the integrated intensity of the $4f5d$ emission, $I_1$, can be expressed as

$$I_1 = \eta_1 \gamma_1 \int_0^{t_p} e^{-\gamma_1 t} dt + \int_0^{t_p} n_1(t) dt$$

$$= \eta_1 F \sigma_0 N_0 \frac{\gamma_1 + (F \sigma_1 - \gamma_1) e^{-F \omega_p}}{F_1 - F_0}$$

$$\quad \times \frac{F_1}{F_0} . \quad (6)$$

Without the UV pulse, the integrated intensity of the $3P_0$ emission is given by $I_0 = \eta_0 N_0$, therefore,

$$\Delta I_0 = I_0 - I'_0 = \frac{F \sigma_0}{F_0} (1 - e^{-F \omega_p}), \quad (7)$$

and

$$\frac{I_1}{\Delta I_0} = \eta_1 \frac{\gamma_1 + (F \sigma_1 - \gamma_1) e^{-F \omega_p} - F_0 (\gamma_1 + F \sigma_1 e^{-F \omega_p}) / F_1}{\eta_0 (F_1 - F_0) (1 - e^{-F \omega_p})} . \quad (8)$$

Equation (7) can be used to find the photon flux density. Equation (8) can be simplified in two extreme cases: (1) $F_1 t_p \ll 1$ and $F \omega_p \ll 1$. This corresponds to the weak excitation or short pulse limit; Eq. (8) can be approximated to $R = I_1 / \Delta I_0 = \eta_1 / \eta_0$. The ratio will not be affected by ESA (the branch ratios will be taken into account in specific calculations). (2) $F_1 t_p \gg 1$ and $F \omega_p \gg 1$. This is the case of a strong excitation limit. Eq. (8) becomes $R = I_1 / \Delta I_0 = \eta_1 \gamma_1 / \eta_0 F_1$. The ratio or the QE measurement will be intensity dependent. More generally, let $y = \gamma_1 / F_1$ and $x = F_1 / F_0$, Eq. (8) can be rewritten as follows:

$$\eta_1 \eta_0 (y = 1) = \frac{(x - 1) (1 - e^{-F \omega_p})}{y(x - 1) - (xy - 1) e^{-F \omega_p} + (1 - y) e^{-F \omega_p}} , \quad (9)$$

where $\eta_1(y = 1) = \eta_0 I_1 / \Delta I_0$, corresponding to the weak excitation limit. For the CAO:Pr sample, $\eta_1 = 4.2\%$ without counting the effect of ESA. Now, we will estimate the flux intensity and take ESA into account. Based on our data, $I_1 / \Delta I_0 = 0.3324$, $\gamma_0 = 6.7 \times 10^7$ s$^{-1}$, and $t_p = 5 \times 10^{-9}$ s, $F \sigma_0$ can be estimated from Eq. (7) to be a value of $8.08 \times 10^7$ s$^{-1}$. $\sigma_0$ has a value of $8 \times 10^{-19}$ cm$^2$, yielding $F = 1 \times 10^{20}$ s$^{-1}$ cm$^{-2}$, corresponding to a power density of 50 MW cm$^{-2}$. Assuming $\sigma_1 = 1 \times 10^{-17}$ cm$^2$ (Ref. 10) and $\gamma_1 = 6.7 \times 10^7$ s$^{-1}$, we have $y = 0.06$, $x \sim 13$. The calculation according to Eq. (9) suggests that the actual QE should be 4.5 times greater than the value we measured. When the power is lowered, there is no substantial difference observed since the intensity dependence of QE becomes less sensitive. The lower power also yields very weak up-converted emission, reducing the signal-to-noise ratio. However, it was difficult to increase power without damaging the sample so that the prediction could be test. Even if the effect of ESA is counted, the QE is still far below a unity observed in other crystals.10 This indicates that the trap centers play a dominant role in the decay of the lowest $4f5d$ state.

We have demonstrated a method for measuring the quantum efficiency of emission using the two-step excitation and the difference of the integrated emission intensities in Pr$^{3+}$:CaAl$_2$O$_7$ and Pr:SaAl$_2$O$_7$ crystals. Deep UV emissions from the lowest $4f5d$ state are detected using two-photon stepwise excitation. The quantum efficiencies of the emission in the two crystal systems have been estimated in the range of $2\%$–$9\%$ at room temperature. The effect of ESA of the lowest $4f5d$ on the quantum efficiency measurement is analyzed, suggesting that, at strong excitation, the actually quantum efficiency may be much higher than the measured values.

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