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Photon cascade emission and quantum efficiency of the $^3P_0$ level in Pr^{3+}-doped $SrAl_{12}O_{19}$ system

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Abstract

Photon cascade emission has been reported in Pr^{3+}-doped $SrAl_{12}O_{19}$ system, providing a unique method for direct measuring the quantum efficiency of $^3P_0$ in this material. The $^1S_0 \rightarrow {}^1I_6$ fluorescence intensity can be taken as a measure of the initial $^3P_0$ population. Thus the quantum efficiency of $^3P_0$ can be calculated using the intensity ratio of the total emission from $^3P_0$ and the emission of $^1S_0 \rightarrow {}^1I_6$. The efficiency decreases as the concentration of Pr increases, indicating the effect of concentration quenching. The quantum efficiency is still substantially less than 100% even in dilute sample due to the thermal excitation of $^1I_6$ and $^3P_1$ states.

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Keywords: $SrAl_{12}O_{19}$; Quantum efficiency; Praseodymium; Cascade emission

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1. Introduction

The optical properties of $^1S_0$ state of Pr^{3+} have been studied as early as in 1970s [1,2]. This state has attracted attention recently due to the potential applications in quantum cutting [3,4]. In some hosts, $^1S_0$ state lies below the lowest 4f5d state. Electrons excited to the 4f5d states relax to $^1S_0$ state and yield photon cascade emission [5,6]. Some of these Pr^{3+}-doped phosphors may have radiative quantum efficiency (QE) higher than 100% under excitation with ultraviolet or vacuum ultraviolet and are applicable to mercury-free lamps and other plasma display devices.

The relative positions of $^1S_0$ state and the lowest 4f5d state depend on the center of gravity and the splitting of the 4f5d configuration. In general, for ionic crystals, the center of gravity of the 4f5d states lies in the vacuum ultraviolet region and decreases in energy as the covalent contribution increases. On the other hand, the splitting of the 4f5d states depends on the strength of crystal field. For typical ionic crystals, fluorides, for example, the $^1S_0$ state is lower than the lowest 4f5d state. It was found recently that in certain cases, such as $LaMgB_5O_{10}$ and $SrAl_{12}O_{19}$, the $^1S_0$ state also lies below the 4f5d states. This is because the Pr ions occupy high coordination sites and experience a

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weaker crystal field environment. Photon cascade emission has been reported in these phosphors [7,8].

In this paper, we investigated the optical properties of $SrAl_{12}O_{19}:Pr^{3+}$ and determined the QE of $^3P_0$ state exploiting the photon cascade emission.

2. Experimental

The $SrAl_{12}O_{19}$:Pr,Mg single crystal fibers (length = 1.0 cm, diameter = 0.7–1.0 mm) were prepared by the laser heated pedestal growth method (LHPG) [9]. Trivalent Pr^{3+} was doped to replace divalent Sr^{2+} ions in the host. A similar amount of Mg^{2+} was co-doped to substitute for Al^{3+} ions for charge compensation purposes. The fluorescence measurements were taken using a Jobin Yvon-Spex FluroMax 2 spectrofluorimeter with a resolution of 0.3 nm.

3. Results and discussion

3.1. Optical properties of $SrAl_{12}O_{19}$:Pr,Mg

Fig. 1 shows the emission spectrum of $SrAl_{12}O_{19}$:0.5%Pr,0.5%Mg excited at 444 nm ($^3H_4 \rightarrow {}^3P_2$) and at room temperature. The intensity has been calibrated and is proportional to the detected photon numbers. Peaks A through G correspond to the $^3P_0 \rightarrow {}^3H_4$, $^3P_1 \rightarrow {}^3H_5$, $^3P_0 \rightarrow {}^3H_5$, $^3H_6$, $^3F_2$, $^3F_3$, $^3F_4$ transitions, respectively. Fig. 2 depicts the emission spectrum excited at 204 nm. Peaks A through E correspond to the following transitions, $^1S_0 \rightarrow {}^3F_4$, $^1G_4$, $^1D_2$, $^1I_6$, and $^3P_0 \rightarrow {}^3H_4$, respectively [10].

Fig. 3 represents the excitation spectra (monitoring the 401 nm ($^1S_0 \rightarrow {}^1I_6$) emission) of $SrAl_{12}O_{19}$:1.0%Pr,1.0%Mg obtained at both room temperature (dashed line) and 77 K (solid line). When the temperature increases from 77 K to room temperature, the absorption edge (as pointed with arrows) red-shifts 5 nm, while the absorption peak at 215.1 nm due to $^3H_4 \rightarrow {}^1S_0$ transition remains unchanged.

3.2. QE of $^3P_0$ state

The radiative QE for an energy state of rare earth ions can be estimated by the ratio of the measured value of fluorescent lifetime of the state and the value calculated by Judd-Ofelt theory. The processes of photon cascade emission provide a unique method for the direct measurement of the QE for the intermediate state yielding the second

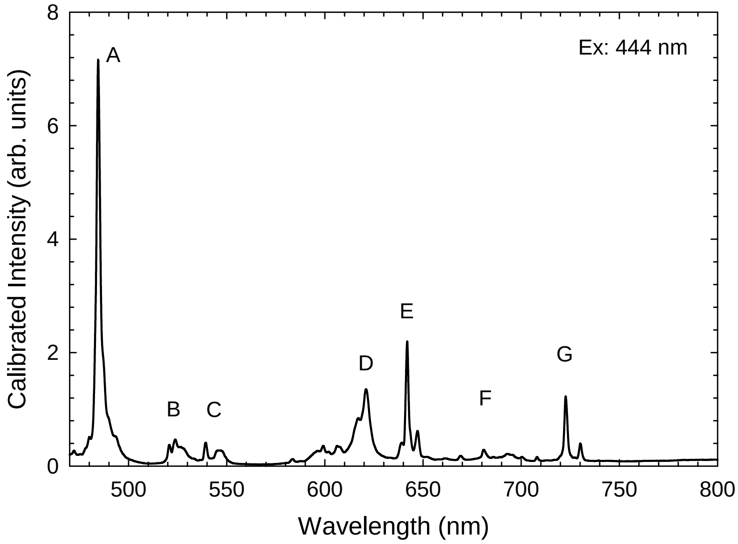

Fig. 1. Emission spectrum of $SrAl_{12}O_{19}$: 0.005 Pr, 0.005 Mg at room temperature with the excitation at 444 nm.

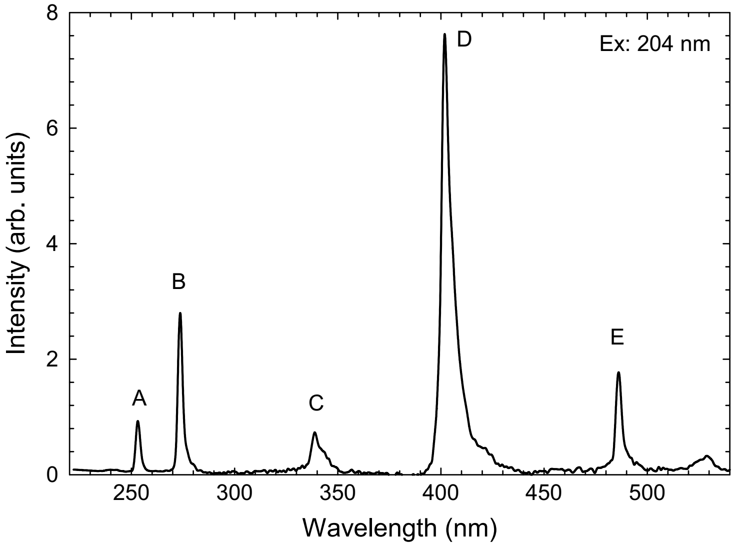

Fig. 2. Emission spectrum of $SrAl_{12}O_{19}$:0.05 Pr, 0.05 Mg at room temperature excited by 204 nm.

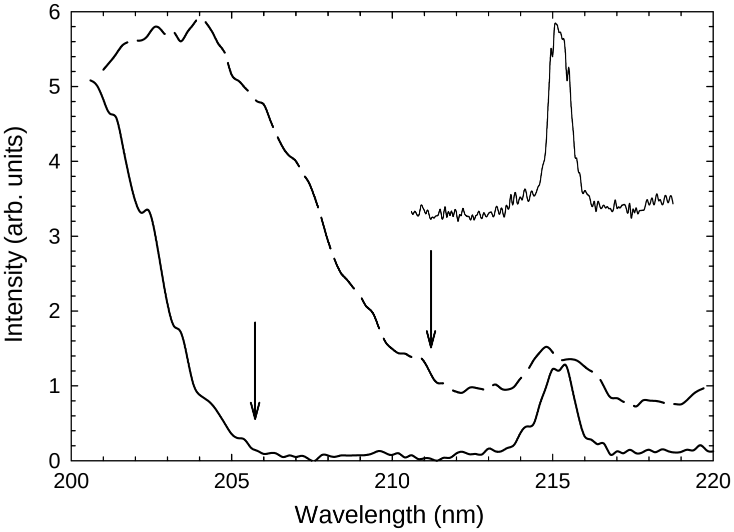

Fig. 3. Excitation spectrum of $SrAl_{12}O_{19}$:0.01 Pr, 0.01 Mg at room temperature (dotted line) and 77 K (solid line). $^1S_0 \rightarrow {}^1I_6$ emission was monitored. Inset: $^1S_0$ peak at 77 K that is independent of temperature.

step emission (the measurement of QE for the initial state of a cascade emission has been demonstrated in Ref. [11]). The QE of $^1G_4$ in Pr^{3+} doped glass ceramics has been directly measured using the intensity ratio of $^1D_2 \rightarrow {}^1G_4$ and $^1G_4 \rightarrow {}^3H_5$ [12,13]. $^3P_0$ in $SrAl_{12}O_{19}$:Pr^{3+} is such an intermediate state when 4f5d states is excited and produces an initial emission from the $^1S_0$ state. Since the splittings between the Stark levels of $^1I_6$, $^3P_1$, and subsequently $^3P_0$ states are small, it is reasonable to assume that the depopulation of $^1I_6$ is dominated by multiphonon relaxation, i.e., all the electrons from $^1S_0$ down to $^1I_6$ will quickly relax to $^3P_0$. The $^1S_0 \rightarrow {}^1I_6$ fluorescence intensity can be taken as a measure of the initial $^3P_0$ population. Thus the QE, η, of $^3P_0$ can be

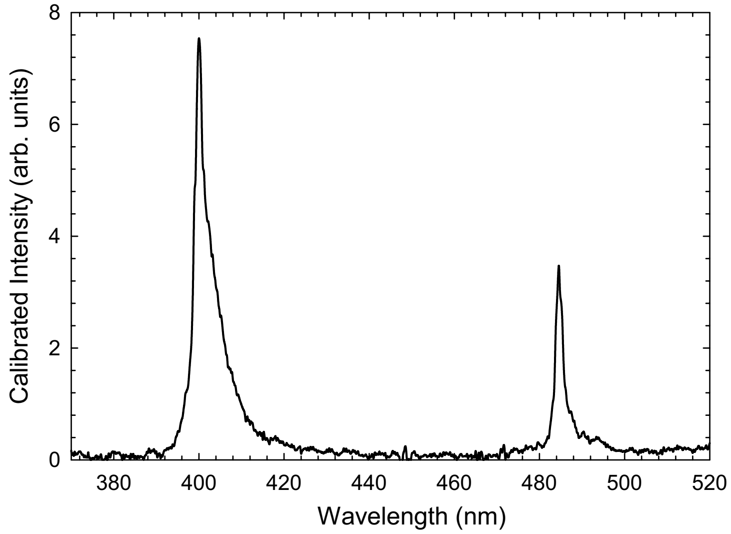

Fig. 4. Emission spectrum of $SrAl_{12}O_{19}$:0.01 Pr, 0.01 Mg at room temperature. The excitation wavelength is at 205 nm ($^3H_4$–4f5d band) with a spectral resolution of 1 nm.

Table 1
Emission QE of $^3P_0$ at room temperature

Host	$SrAl_{12}O_{19}$				$CaAl_{12}O_{19}$
Pr concentration	0.005	0.01	0.05	0.10	0.01
$R=I(^3P_0-^3H_4)/I(^1S_0-^1I_6)$	0.291	0.27	0.189	0.104	0.326
β	0.43	0.43	0.40	0.34	0.412
η	0.68	0.64	0.47	0.31	0.79

written as

$$\begin{aligned}\eta(^3P_0) &= \frac{\text{Number of photons emitted from } ^3P_0}{\text{Number of electrons relaxed to } ^3P_0}\\ &= \frac{\text{Total intensity from } ^3P_0}{\text{Intensity of the emission } ^1S_0 \rightarrow {}^1I_6}\\ &= \frac{I(^3P_0 -^3 H_4)}{\beta I(^1S_0 -^1 I_6)} = \frac{R}{\beta}, \qquad (1)\end{aligned}$$

where β is the branching ratio of the $^3P_0 \rightarrow {}^3H_4$ transition and R the intensity ratio of $^3P_0 \rightarrow {}^3H_4$ and $^1S_0 \rightarrow {}^1I_6$. β can be obtained from Fig. 1 by neglecting the infrared transitions, $^3P_0 \rightarrow {}^1G_4$, $^1D_2$, which entail less than 4% of the total intensity estimated by Judd-Ofelt theory [14].

Fig. 4 shows the emissions, $^1S_0 \rightarrow {}^1I_6$ and $^3P_0 \rightarrow {}^3H_4$, of $SrAl_{12}O_{19}$:1.0% Pr,1.0% Mg sample excited at 205 nm, where the ratio R can be readily obtained. All the results and calculations are listed in Table 1. The data for $CaAl_{12}O_{19}$ are also listed in the table for comparison. The QE of $^3P_0$ decreases as the Pr^{3+} concentration increases due to the concentration quenching. However, the QE is significantly less than 1 even at the low concentration (0.5%).

The low QE at room temperature can be attributed to thermal excitation of the $^1I_6$ and $^3P_0$ states. In fact, in the spectrum measured at room temperature, we do observe $^3P_1 \rightarrow {}^3H_5$ emission peaking at 525 nm (peak B in Fig. 1). Further investigation shows that the population in $^1I_6$ state is about $\frac{1}{3}$ of that in $^3P_0$ at room temperature. Infrared emissions, $^1I_6 \rightarrow {}^1G_4$ and $^3P_0 \rightarrow {}^1G_4$, have been observed. $^1I_6 \rightarrow {}^1G_4$ disappears at 77 K, yielding the QE of $^3P_0$ state close to 100%. The results and detailed Judd-Ofelt analysis is to be published elsewhere.

Several other possibilities that may account for the low QE of $^3P_0$ state can be excluded: (1) Thermal quenching: At room temperature, there is no $^1D_2$ emission observed from $SrAl_{12}O_{19}$:Pr,Mg when $^3P_0$ is excited, which is in contract to $LaMgB_5O_{10}$:Pr [7]. At 77 K, the radiative decay time of $^3P_0$ state (1.0 at% Pr^{3+} sample) changes slightly from that at room temperature. Both results indicate that the thermal quenching due to the multi-phonon relaxation is negligible. (2) Concentration quenching: Concentration quenching due to the cross-relaxation of $^3P_0$ ions may exist in the 5 and 10 at% samples. Lifetimes of $^3P_0$ state of these samples decrease at higher temperature, suggesting phonon involvement in the cross-relaxation process. However, as discussed in thermal quenching, the decay time of $^3P_0$ state for the 1.0 at% sample is nearly independent on the temperature, showing that the effect of concentration quenching on the QE at that concentration can be neglected. (3) Excited state absorption: The electrons in $^3P_0$ state can return to the 4f5d band when they absorb 205 nm excitation. Based on a cross section of excited state absorption for the $^3P_0$ state, $\sigma = 10^{-17}\,\mathrm{cm}^2$ [15], and a decay time $\tau = 30\,\mu\mathrm{s}$, an excitation with a photon flux density equal to $1/(\sigma\tau) = 3.3 \times 10^{21}\,\mathrm{s}^{-1}\,\mathrm{cm}^{-2}$ or a power density $= 10^3\,\mathrm{W\,cm}^{-2}$ is needed to make excited state absorption of $^3P_0$ state comparable to its emission. The excitation used in the experiment is made lower than this value and cannot affect the QE through excited state absorption.

In summary, we have measured the QE of $^3P_0$ state in $SrAl_{12}O_{19}$:Pr,Mg system using photon cascade emission. At higher concentrations, the QE is lower mainly due to the concentration quenching. At lower concentrations, thermal excitation of $^3P_0$ and $^1I_6$ plays an important role in lowering the QE.

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