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Absorption and fluorescence spectra of Pr^{3+} in YPO_4 ☆

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Abstract

Results of spectroscopic measurements of YPO_4:Pr^{3+} are reported. Based on these results, the fluorescent lines were identified. It is confirmed that the 612.8 nm emission line is due to $^1D_2(\Gamma_3)\rightarrow{}^3H_4(\Gamma_5)$ transition of Pr^{3+}. It is found that the fluorescence lines from $^1D_2$ are dominant for samples of low Pr^{3+} concentration when $^3P_0$ is selectively excited, which indicated very efficient relaxation from $^3P_0$ to $^1D_2$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: YPO_4:Pr^{3+}; Decay curve; Fluorescence

1. Introduction

As a representative of rare earth orthophosphate, YPO_4 is a kind of important luminescent host. Related studies have been flourishing since the 1980s. Trivalent ion Pr^{3+} attracted considerable attention in recent years for the interesting fluorescent features such as upconversion and UV emission [1,2]. But there is still something not very clear about spectra characters of YPO_4:Pr^{3+}, such as, the assignment of 612.8 nm emission line [3]. In this work, spectroscopic measurements of YPO_4:Pr^{3+} are presented. The assignment of the fluorescent lines are discussed. The doubtful 612.8 nm line is confirmed to be due to $^1D_2(\Gamma_3)\rightarrow{}^3H_4(\Gamma_5)$ transition. Concentration dependence of the Pr^{3+} fluorescence is also analyzed. It is found that emissions originating from $^1D_2$ level of Pr^{3+} are very strong with a selective excitation on $^3P_0$ level. In low Pr^{3+} concentration samples, $^1D_2$ emissions are much more stronger than the emissions from $^3P_0$ level. Relative excitation relaxation process is discussed.

2. Experimental

YPO_4:Pr^{3+} powder was prepared by solid state reaction method or coprecipitation method. For different Pr^{3+} concentration samples, excitation spectra, visible emission spectra at different temperature, transmission spectra and decay curve measurements were performed. Transmission spectra were scanned on a GDM1000 Carl Zeiss grating double monochrometer. In other cases, excitation was provided by pulsed radiation from a dye laser pumped with a frequency-tripled YAG:Nd^{3+} laser. The dye used in this work is Coumarin 500. Fluorescence from the sample was collected into a HRS2 Jobin-Yvon monochrometer and detected with a R374 Hamamatsu photomultiplier tube. The decay curve measurements were realized using a Lecroy 9410 oscilloscope interfaced with a computer.

3. Results

Fig. 1 is a typical room temperature transmission spectrum of YPO_4:$Pr^{3+}_{0.01}$ from which the positions of some energy levels are determined, Table 1. According to the excitation spectra, dye laser was tuned to 489.4 nm in resonance with a $^3H_4$ ground state to $^3P_0$ transition of Pr^{3+}. At room temperature, strong red fluorescence originates from the f–f transitions of Pr^{3+} in different concentration samples was observed. The fluorescence spectra are shown in Fig. 2. Major emissions can be divided into four groups: (1) 596.0, 597.4, 600.9, 601.9 nm, (2) 612.8 nm, (3) 617.6, 618.8 nm, and (4) 648.0, 650.0 nm. The intensities of groups (3) and (4) increase linearly with the increase of Pr^{3+} concentration. At the same time, the intensities of groups (1) and (2) change slightly. For all the samples, when the temperature is reduced, the line width

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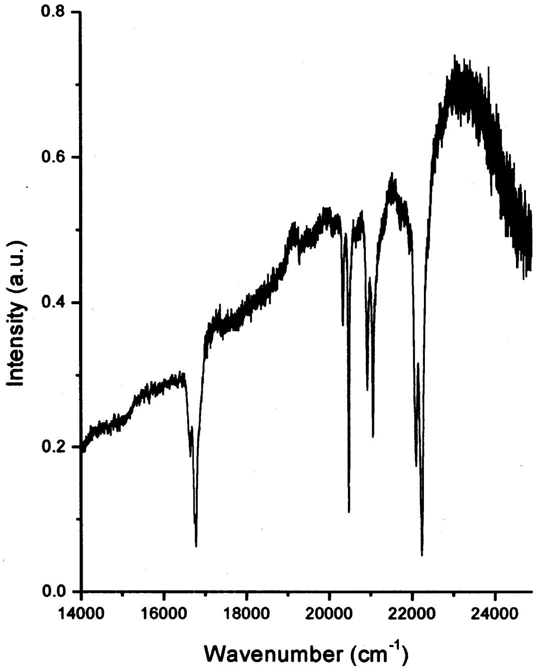

Fig. 1. Transmission spectrum of $YPO_4:Pr^{3+}_{0.01}$ at room temperature.

Table 1
Transitions energy between some levels in $YPO_4:Pr^{3+}$ determined by the transmission spectrum

	$^3P_2(\Gamma_1)$	$^3P_1(\Gamma_5)$	$^3P_0(\Gamma_5)$	$^1D_2(\Gamma_5)$
$^3H_4(\Gamma_4)$ (cm^{-1})	22 235	21 059	20 477	16 783
$^3H_4(\Gamma_5)$ (cm^{-1})	22 101	20 926	20 346	16 653

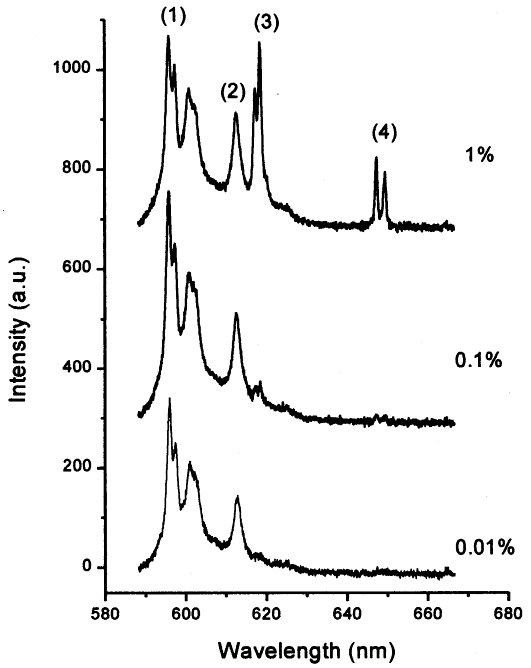

Fig. 2. Concentration dependence of room temperature emission spectra of $YPO_4:Pr^{3+}_{0.01}$.

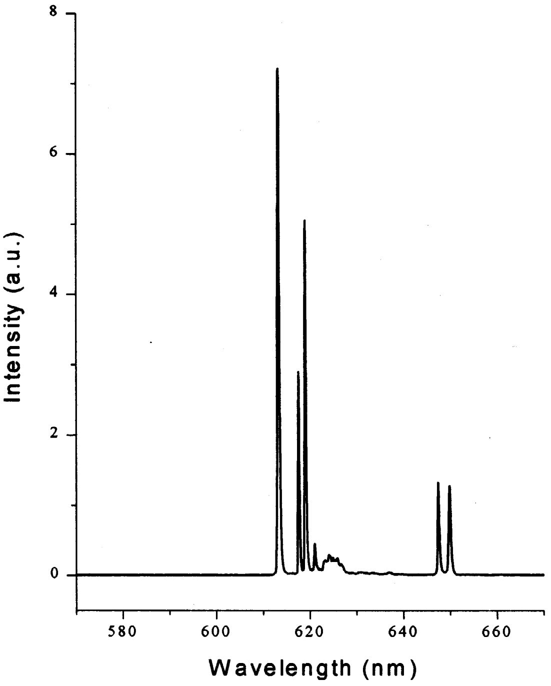

Fig. 3. Emission spectra of $YPO_4:Pr^{3+}_{0.01}$ at 12 K.

becomes narrower and the intensity of group (1) decreases. At 12 K, group (1) is not observed as shown in Fig. 3.

Decay curves were recorded to measure the lifetimes of corresponding levels. In Fig. 4(a), transitions in groups (3) and (4) decay in the single exponential way with $t_1=0.66$ μs. Decay curves of transitions in groups (1) and (2) are shown in Fig. 4(b) with $t_2=0.07$ ms.

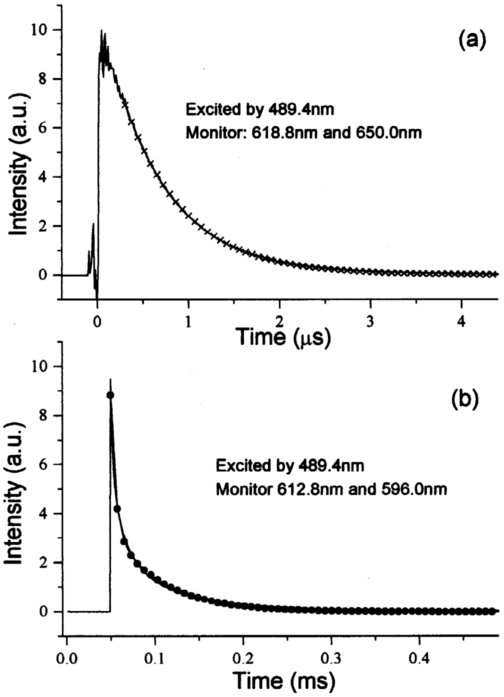

Fig. 4. Decay curves of (a) $^3P_0$ emissions and (b) $^1D_2$ emissions of $YPO_4:Pr^{3+}_{0.01}$ at RT.

4. Discussion

Considering the results of absorption spectrum and the energy levels' positions [3], most transitions are identified as shown below: (1) $^1D_2(\Gamma_5, \Gamma_1) \rightarrow {}^3H_4(\Gamma_4, \Gamma_5)$, (3) $^3P_0(\Gamma_1) \rightarrow {}^3H_4(\Gamma_4, \Gamma_5)$ and (4) $^3P_0(\Gamma_1) \rightarrow {}^3F_2(\Gamma_4, \Gamma_5)$. The 612.8 nm (16319 cm^{-1}) line for group (2) cannot be assigned directly, as the energy does not correspond closely with any transitions between levels. It was guessed to be emission from the lowest crystal field level of $^1D_2$ multiplet to one of the ground levels [$^1D_2(\Gamma_3) \rightarrow {}^3H_4(\Gamma_5)$] [3]. This transition is allowed but the transition between $^1D_2(\Gamma_3)$ and the lowest level $^3H_4(\Gamma_4)$ is forbidden by the selection rules. Two facts support this identification: its lifetime and the concentration dependence of the spectra are the same as group (1).

At room temperature, we can see absorption from $^3H_4(\Gamma_5)$ state Fig. 1, but there is no corresponding line for $^3H_4(\Gamma_5) \rightarrow {}^1D_2(\Gamma_3)$ transition in the absorption spectrum. The reason can be explained as follows. The intervals between $^1D_2(\Gamma_3)$ level and $^1D_2(\Gamma_5, \Gamma_1)$ level are 282 cm^{-1} and 332 cm^{-1}. The population on $^1D_2(\Gamma_3)$ level, according to Boltzmann factor, is about five times of the population on $^1D_2(\Gamma_5)$ and $^1D_2(\Gamma_1)$ level at room temperature. Since the fluorescence of group (1) is stronger than that of group (2), we can conclude that the transition rate of $^1D_2(\Gamma_3)$ level is much less. In addition, there is a 139 cm^{-1} interval between $^3H_4(\Gamma_5)$ state and the lowest one $^3H_4(\Gamma_4)$. This means the population on $^3H_4(\Gamma_4)$ is twice that on $^3H_4(\Gamma_5)$ state, consequently the $^3H_4(\Gamma_5) \rightarrow {}^1D_2(\Gamma_3)$ absorption should be much weaker and hardly to be observed.

The temperature dependence of the emission spectra was also consistent with this explanation. The intensity of group (1) decreases with the decrease of temperature, which is due to the fact that the population on Γ_5 and Γ_1 level reduced at low temperature. At 12 K, since there is almost no Pr^{3+} ion on $^1D_2(\Gamma_5)$ and $^1D_2(\Gamma_1)$ level, group (1) was not observed at all, Fig. 3.

There is another prominent feature of the fluorescence for $YPO_4:Pr^{3+}$. The lifetime of $^3P_0$ state of Pr^{3+} in YPO_4 is so short as to 0.66 μs instead of around 12 μs in most other hosts [5] and the intensities of $^3P_0$ emissions are much weaker than emissions from $^1D_2$ in low Pr^{3+} concentration samples (below 0.1%) although we excited $^3P_0$ state selectively. This indicates that the $^3P_0 \rightarrow {}^1D_2$ relaxation are very efficient. Since the maximum phonon energy is very high (1058 cm^{-1}) in YPO_4 [4] while the gap between $^3P_0$ and $^1D_2$ levels is about 4000 cm^{-1}, the $^3P_0 \rightarrow {}^1D_2$ nonradiative transition need only four phonons. However, the maximum phonon energy is only 260 cm^{-1} in $LaCl_3$, so the decay of $^3P_0$ in YPO_4 is much faster than in $LaCl_3$. That is why emissions from $^1D_2$ of Pr^{3+} in YPO_4 are very strong under selective $^3P_0$ excitation. When the concentration of Pr^{3+} increases ten times (from 0.01 to 1%), the relative intensity of $^1D_2$ emissions do not increase while that of $^3P_0$ emissions increase ten times. It seems that the concentration quenching of $^1D_2$ emissions occurs when there is only about 0.1% Pr^{3+} ions in the sample.

5. Conclusion

In conclusion, under selective $^3P_0$ excitation on $YPO_4:Pr^{3+}$, all the fluorescent transitions are identified, especially the 612.8 nm line in group (2) is attributed to $^1D_2(\Gamma_3) \rightarrow {}^3H_4(\Gamma_5)$ transition of Pr^{3+}. Due to the high phonon energy in YPO_4, the nonradiative relaxation of $^3P_0 \rightarrow {}^1D_2$ is very efficient,which results fast decay of $^3P_0$ level and strong emission originating from $^1D_2$ level. Concentration dependence of the spectra indicates that the quenching of $^1D_2$ level appears at low Pr^{3+} concentration in YPO_4.

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