



Energy transfer in Pr^{3+} - and Cr^{3+} -codoped $\text{SrAl}_{12}\text{O}_{19}$ system

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Abstract

The energy transfer processes in Pr^{3+} - and Cr^{3+} -codoped $\text{SrAl}_{12}\text{O}_{19}$ system are studied experimentally. The transfer can convert the $^1\text{S}_0$ ultraviolet fluorescence of Pr^{3+} into the red emission of Cr^{3+} . The $^3\text{P}_0$ state, which may be populated by $^1\text{S}_0 \rightarrow ^1\text{I}_6$ emission, can also act as a donor state in the transfer to Cr^{3+} . Cross-relaxation process is reported firstly in energy transfer between the pair of Pr^{3+} – Cr^{3+} in $\text{SrAl}_{12}\text{O}_{19}$ system. Two-step energy transfer is discussed, which involves two visible photons for each vacuum ultraviolet photon absorbed.

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1. Introduction

Photon cascade emission (PCE), which converts vacuum ultraviolet (VUV) excitation to visible emission with quantum efficiency higher than 100%, is an attractive feature for lamps and plasma display panels. This PCE type of luminescence can be observed when Pr^{3+} is doped in certain hosts in which the lowest 4f5d band lies

above the $^1\text{S}_0$ state of the $4f^2$ configuration. Electrons excited to the 4f5d states relax to $^1\text{S}_0$ state and yield photon cascade emission [1,2]. Emission from the $^1\text{S}_0$ state to the $^1\text{I}_6$ level results in the first photon of the PCE process. A second transition that connects the upper $^3\text{P}_0$ state with several ground-state levels yields the second photon (see the left part of Fig. 1). By now, more than a dozen of such Pr^{3+} -based PCE phosphors have been identified and studied in detail [3] but found useless for application because about half of the visible light comes from $^1\text{S}_0 \rightarrow ^1\text{I}_6$ transition

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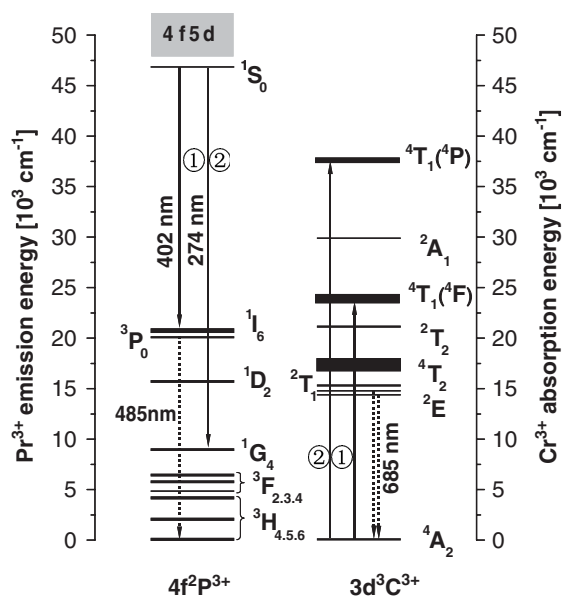


Fig. 1. Part of the energy level scheme of Pr^{3+} (left) and Cr^{3+} (right) in SAO. The anticipated transitions involved in cross-relaxation from Pr^{3+} to Cr^{3+} are indicated.

that generally falls in deep violet. The chromaticity of the emission is not optimal for phosphor applications. In addition, the intensity of $^1\text{S}_0 \rightarrow ^1\text{G}_4$, $^3\text{F}_4$ ultraviolet (UV) emission is usually comparable to that of $^1\text{S}_0 \rightarrow ^1\text{I}_6$ emission or even stronger in some hosts, thus also reducing the visible emission.

The purpose of this work is to search for a codoped system that can convert the UV or deep violet of Pr^{3+} radiation into the visible through energy transfer processes. We have chosen Cr^{3+} as a codopant because of its efficient red emission and because many absorption transitions of Cr^{3+} overlap the $^1\text{S}_0$ emission (see right part of Fig. 1). We have observed energy transfer from Pr^{3+} to Cr^{3+} in the Pr^{3+} - and Cr^{3+} -codoped $\text{SrAl}_{12}\text{O}_{19}$ system and observed conversion of the $^1\text{S}_0$ UV and $^3\text{P}_0$ blue fluorescence into red emission.

2. Experimental

$\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$ (SAO: Pr), $\text{SrAl}_{12}\text{O}_{19}:\text{Cr}^{3+}$ (SAO: Cr) and $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}, \text{Cr}^{3+}$ (SAO: Pr,

Cr) phosphors were synthesized by solid-state reaction. The obtained polycrystalline samples were checked to be single phase by X-ray diffraction. The trivalent Pr^{3+} ions replace divalent Sr^{2+} ions in the host and appropriate amount of Mg^{2+} was codoped substituting for Al^{3+} ions for charge compensation. Considering charge neutrality and ion size, trivalent Cr^{3+} ions substituting for Al^{3+} enter the host.

All the measurements were performed at room temperature (RT). The VUV excitation spectra were measured by using a VUV monochromator. The excitation and emission spectra in the UV region were obtained by Hitachi F-4500 fluorescence spectrophotometer.

3. Results and discussions

Fig. 2 shows the emission spectrum of Pr^{3+} (below) and the excitation spectrum of Cr^{3+} (up). The emission of SAO: Cr (inset) consists of a $^2\text{E}(^4\text{F}) \rightarrow ^4\text{A}_2(^4\text{F})$ zero-phonon transition (R-lines) peaking at 685 nm and some vibronic sidebands [4]. From Fig. 2, it follows that two favorable spectral overlaps exist. One is between the $^1\text{S}_0 \rightarrow ^1\text{I}_6$

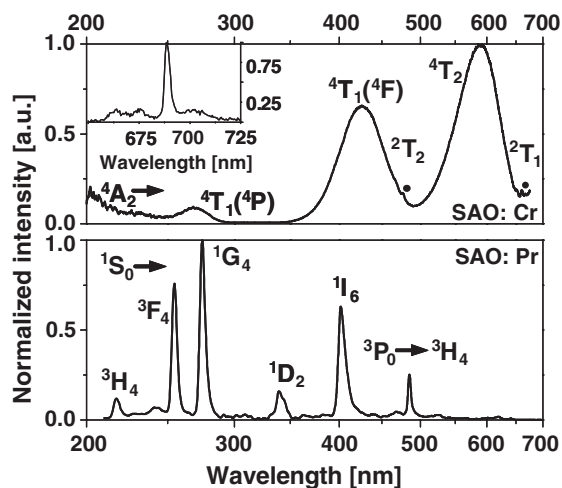


Fig. 2. Emission spectra of SAO: Pr (below) upon Pr^{3+} 4f5d states excitation around 199 nm and excitation spectra (up) of SAO: Cr, monitoring the R-lines emission of Cr^{3+} at 685 nm. Emission spectra of SAO: Cr (inset) at Cr^{3+} $^4\text{T}_1(^4\text{P})$ state excitation about 270 nm.

Pr³⁺ emission and $^4A_2(^4F) \rightarrow ^4T_1(^4F)$ Cr³⁺ absorption, the other is between $^1S_0 \rightarrow ^3F_J$ Pr³⁺ emission and $^4A_2(^4F) \rightarrow ^4T_1(^4P)$ Cr³⁺ absorption. The two spectral overlaps could promote energy transfer between Pr³⁺ in the 1S_0 state and Cr³⁺ in the 4A_2 ground state through cross-relaxation. It must be noted that the Pr³⁺ $^3P_0 \rightarrow ^3H_4$ emission at 485 nm also has partial spectral overlap with Cr³⁺ absorption. So the 3P_0 state, which may be populated by $^1S_0 \rightarrow ^1I_6$ emission, can also act as a donor state in the transfer to Cr³⁺. Upon excitation in Pr³⁺ $4f5d$ states, there are two principal two-step routes (indicated by ① and ② in Fig. 1) for energy transfer from Pr³⁺ 1S_0 state to Cr³⁺. For route ①, the first step result in Cr³⁺ in the $^4T_1(^4F)$ excited states and Pr³⁺ in the 1I_6 state through cross-relaxation. In the second step, the Cr³⁺ returns to the ground by emitting a red photon. The Pr³⁺ ion in the 1I_6 state relax to the 3P_0 state [5], and then the 3P_0 state gives a blue emission or transfers partial excitation energy to a second Cr³⁺ ion, which also results in a red emission. Therefore, if cross-relaxation occurs, the route ① will involve two visible photons for each VUV photon absorbed. For route ②, the first step result in Cr³⁺ in the $^4T_1(^4P)$ excited states and Pr³⁺ in the 1G_4 state. Similarly, in the second step, Cr³⁺ returns to the ground by emitting a red photon, while the emission lines of Pr³⁺ in the 1G_4 state located in infrared region. So the route ② only involves one visible photon. In the present work, we only focus on the route ①. In addition, Pr³⁺ 1S_0 state also has the possibility of direct energy transfer to Cr³⁺, which will only populate the higher states of Cr³⁺ and result in R-lines emission.

Fig. 3(a) presents the excitation spectra of the R-lines emission in SAO: 1%Cr, x%Pr (x = 0, 1, 3, 5, 7). All excitation spectra of Cr³⁺ are scaled on the $^4A_2 \rightarrow ^4T_1(^4F)$ excitation intensity. Clearly, except for the peaks of Cr³⁺ $^4A_2 \rightarrow ^2T_2$ (476 nm), the peaks of Pr³⁺ $^3H_4 \rightarrow ^3P_0$ (485 nm) is also found clearly in the excitation spectra. Fig. 3(b) plots the emission spectra of Cr³⁺ in SAO: 1%Cr, x%Pr (x = 1, 3, 5, 7), excited at 485 nm. The intensity of the excitation peaks of Pr³⁺ $^3H_4 \rightarrow ^3P_0$ transition and the R-lines of Cr³⁺ both increase with increasing Pr³⁺ concentration at fixed Cr³⁺

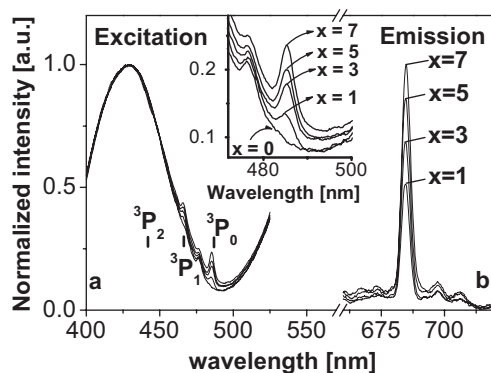


Fig. 3. Excitation spectra of Cr³⁺ in SAO: 1%Cr, x%Pr (x = 0, 1, 3, 5, 7) (left, a) monitoring the R-lines emission of Cr³⁺ at 685 nm. The spectra are normalized by the $^4A_2 \rightarrow ^4T_1(^4F)$ excitation intensity. Emission spectra of SAO: 1%Cr, x%Pr (x = 1, 3, 5, 7) (right, b), excited into 3P_0 state at 485 nm. The vertical lines represent the excitation states energies of Pr³⁺ as observed in SAO: Pr.

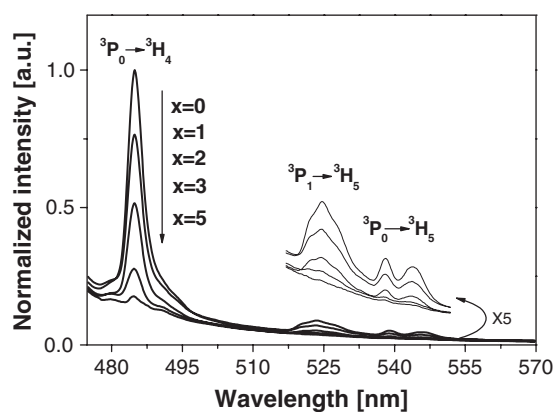


Fig. 4. Emission spectra of SAO: 1%Pr, x%Cr (x = 0, 1, 2, 3, 4), excited into the 3P_2 state of Pr³⁺ at 445 nm.

concentration. The results indicate the occurrence of energy transfer from Pr³⁺ 3P_0 state to Cr³⁺.

Fig. 4 depicts the emission spectra of SAO: 1%Pr, x%Cr (x = 0, 1, 2, 3, 4), excited into the 3P_2 state of Pr³⁺ at 445 nm. All the electrons populated in 3P_2 state will quickly relax to 3P_0 level at RT [5]. The emission at 485 nm is assigned to the $^3P_0 \rightarrow ^3H_4$ transition. The 3P_0 emission intensity decreases greatly with increasing Cr³⁺ concentration. It is also observed that the decay constant of Pr³⁺ 3P_0 decreases as the Cr³⁺ concentration increases. Both the observed variation

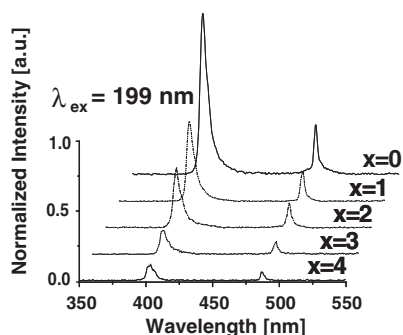


Fig. 5. Emission spectra of Pr^{3+} in SAO: 1%Pr, $x\%$ Cr ($x = 0, 1, 2, 3, 4$), excited at 199 nm.

of spectral properties and the dynamical processes indicate that the energy transfer from $\text{Pr}^{3+} {}^3\text{P}_0$ to Cr^{3+} occurred in the co-doped system.

Emission spectra of Pr^{3+} in SAO: 1%Pr, $x\%$ Cr ($x = 0, 1, 2, 3, 4$), excited at 199 nm, are displayed in Fig. 5. The two emission lines are typical for Pr^{3+} -based PCE phosphors. The emission intensity of the ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$ transition decreases greatly with the increasing of Cr^{3+} concentration, which suggests that there is energy transfer from the $\text{Pr}^{3+} {}^1\text{S}_0$ state to Cr^{3+} .

To investigate whether or not the cross-relaxation for the couple Pr^{3+} – Cr^{3+} , as proposed above, occurs, emission spectra of Pr^{3+} in SAO: 1%Pr, $x\%$ Cr ($x = 0, 1, 2, 3, 4$) upon exciting in 4f5d and ${}^3\text{P}_2$ states are compared in Fig. 6. Because in case the cross-relaxation occurs, a difference in evolution of the ${}^3\text{P}_0$ emission intensity with increasing Cr^{3+} concentrations is expected. This difference has the following origin. As mentioned previously, upon excitation into the 4f5d states of Pr^{3+} , there are two possibilities for energy transfer from $\text{Pr}^{3+} {}^1\text{S}_0$ state to Cr^{3+} . Direct energy transfer can only populate the higher states of Cr^{3+} , while for cross-relaxation, it will feed the $\text{Pr}^{3+} {}^3\text{P}_0$ level except for the excited states of Cr^{3+} . Under excitation into the ${}^3\text{P}_2$ state of Pr^{3+} the cross-relaxation cannot occur, but the energy transfer from ${}^3\text{P}_0$ state to Cr^{3+} will take place and the Cr^{3+} concentration-dependent emission of ${}^3\text{P}_0$ results, as is shown in Fig. 4. In Fig. 6(a), the emission spectra of Pr^{3+} in SAO: 1%Pr, $x\%$ Cr ($x = 0, 1, 2, 3, 4$) under 199 nm excitation have been normalized by the intensity of ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$ transition. The depopulation of ${}^1\text{I}_6$ is

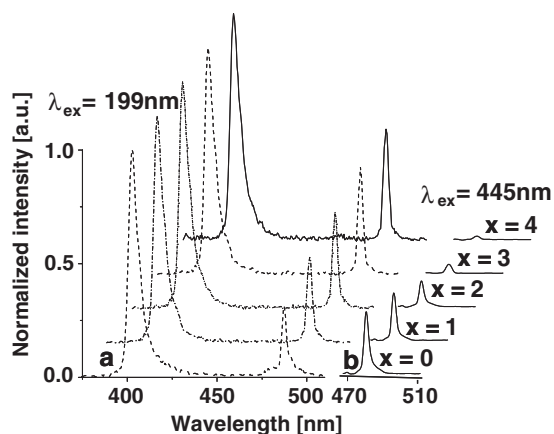


Fig. 6. Emission spectra of Pr^{3+} in SAO: 1%Pr, $x\%$ Cr ($x = 0, 1, 2, 3, 4$), excited at 199 nm, normalized by the intensity of ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$ transition (left, a). Emission spectra of $\text{Pr}^{3+} {}^3\text{P}_0 \rightarrow {}^3\text{H}_4$ transition in SAO: 1%Pr, $x\%$ Cr ($x = 0, 1, 2, 3, 4$), excited into ${}^3\text{P}_2$ state at 445 nm (right, b). The emission intensity of ${}^3\text{P}_0$ state in SAO: 1%Pr at 445 nm excitation has been scaled on the same emission upon 4f5d states excitation.

dominated by multiphonon relaxation, i.e., all the electrons from ${}^1\text{S}_0$ down to ${}^1\text{I}_6$ will quickly relax to ${}^3\text{P}_0$. The ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$ fluorescence intensity can be taken as a measure of the initial ${}^3\text{P}_0$ population [5]. Thus, upon Pr^{3+} 4f5d excitation, when the intensities of ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$ transitions are normalized, the populations of the ${}^3\text{P}_0$ states in SAO: 1%Pr, $x\%$ Cr samples can be considered as the same if the cross-relaxation step cannot occur. In fact, the same population of the ${}^3\text{P}_0$ states can be achieved by excitation into ${}^3\text{P}_2$ states. The emissions of ${}^3\text{P}_0$ states, excited into ${}^3\text{P}_2$ states, have been shown in Fig. 6(b). The emission intensity of ${}^3\text{P}_0$ state in SAO: 1%Pr has been scaled on the same emission upon 4f5d states excitation. Thus, if cross-relaxation cannot occur, due to the second energy transfer step the intensity of the ${}^3\text{P}_0$ emission will decrease absolutely relative to that of ${}^1\text{S}_0$ emission, as displayed in Fig. 6(b) and Fig. 4. But as clearly shown in Fig. 6(a), the ${}^3\text{P}_0/{}^1\text{S}_0$ emission intensity ratio is enhanced slightly upon 4f5d excitation. The enhancing of the ${}^3\text{P}_0 \rightarrow {}^3\text{H}_4$ transition must come from the cross-relaxation because only by cross-relaxation the population of ${}^3\text{P}_0$ state can be reinforced. Therefore, cross-relaxation is involved in the two-step energy transfer.

In conclusion, we have observed energy transfer from both 1S_0 and 3P_0 states of Pr^{3+} to Cr^{3+} . Cross-relaxation process for $Pr^{3+}-Cr^{3+}$ couple in SAO: Pr, Cr system is reported for the first time. Two-step energy transfer occurs, which results in two visible photons for each VUV photon absorbed.

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