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

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Abstract

The energy transfer processes in Pr\(^{3+}\) - and Cr\(^{3+}\) -codoped SrAl\(_{12}\)O\(_{19}\) system are studied experimentally. The transfer can convert the \(1S_0\) ultraviolet fluorescence of Pr\(^{3+}\) into the red emission of Cr\(^{3+}\). The \(3P_0\) state, which may be populated by \(1S_0\) 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 SrAl\(_{12}\)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 \(1S_0\) state of the 4f\(^2\) configuration. Electrons excited to the 4f5d states relax to \(1S_0\) state and yield photon cascade emission [1,2]. Emission from the \(1S_0\) state to the \(1I_6\) level results in the first photon of the PCE process. A second transition that connects the upper \(3P_0\) 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 \(1S_0\rightarrow1I_6\) transition.
that generally falls in deep violet. The chromaticity of the emission is not optimal for phosphor applications. In addition, the intensity of $^{1}S_0 \rightarrow ^{1}I_6$, $^{3}F_4$ ultraviolet (UV) emission is usually comparable to that of $^{1}S_0 \rightarrow ^{1}I_6$ 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 $^{1}S_0$ 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 SrAl$_{12}$O$_{19}$ system and observed conversion of the $^{1}S_0$ UV and $^{3}P_0$ blue fluorescence into red emission.

2. Experimental

SrAl$_{12}$O$_{19}$: Pr$^{3+}$ (SAO: Pr), SrAl$_{12}$O$_{19}$: Cr$^{3+}$ (SAO: Cr) and SrAl$_{12}$O$_{19}$: Pr$^{3+}$, 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 $^2E(^4F) \rightarrow ^4A_2(^4F)$ 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 $^{1}S_0 \rightarrow ^{1}I_6$...
Pr$^{3+}$ emission and $^{4}A_{2}(4F) \rightarrow ^{4}T_{1}(4F)$ Cr$^{3+}$ absorption, the other is between $^{1}S_{0} \rightarrow ^{3}F_{J} Pr^{3+}$ emission and $^{4}A_{2}(4F) \rightarrow ^{4}T_{1}(4P)$ Cr$^{3+}$ absorption. The two spectral overlaps could promote energy transfer between Pr$^{3+}$ in the $^{1}S_{0}$ state and Cr$^{3+}$ in the $^{4}A_{2}$ ground state through cross-relaxation. It must be noted that the Pr$^{3+}$ $^{3}P_{0} \rightarrow ^{3}H_{4}$ emission at 485 nm also has partial spectral overlap with Cr$^{3+}$ absorption. So the $^{3}P_{0}$ state, which may be populated by $^{1}S_{0} \rightarrow ^{1}I_{6}$ emission, can also act as a donor state in the transfer to Cr$^{3+}$. Upon excitation in Pr$^{3+}$ 4f5d states, there are two principal two-step routes (indicated by ① and ② in Fig. 1) for energy transfer from Pr$^{3+}$ $^{1}S_{0}$ state to Cr$^{3+}$. For route ①, the first step result in Cr$^{3+}$ in the $^{4}T_{1}(4F)$ excited states and Pr$^{3+}$ in the $^{1}I_{6}$ state through cross-relaxation. In the second step, the Cr$^{3+}$ returns to the ground by emitting a red photon. The Pr$^{3+}$ ion in the $^{1}I_{6}$ state relax to the $^{3}P_{0}$ state [5], and then the $^{3}P_{0}$ state gives a blue emission or transfers partial excitation energy to a second Cr$^{3+}$ 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 Cr$^{3+}$ in the $^{4}T_{1}(4P)$ excited states and Pr$^{3+}$ in the $^{1}G_{4}$ state. Similarly, in the second step, Cr$^{3+}$ returns to the ground by emitting a red photon, while the emission lines of Pr$^{3+}$ in the $^{1}G_{4}$ 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, Pr$^{3+}$ $^{1}S_{0}$ state also has the possibility of direct energy transfer to Cr$^{3+}$, which will only populate the higher states of Cr$^{3+}$ 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 Cr$^{3+}$ are scaled on the $^{4}A_{2} \rightarrow ^{4}T_{1}(4F)$ excitation intensity. Clearly, except for the peaks of Cr$^{3+}$ $^{4}A_{2} \rightarrow ^{2}T_{2}$ (476 nm), the peaks of Pr$^{3+}$ $^{3}H_{4} \rightarrow ^{3}P_{0}$ (485 nm) is also found clearly in the excitation spectra. Fig. 3(b) plots the emission spectra of Cr$^{3+}$ in SAO: 1%Cr, $x\%$Pr ($x = 1, 3, 5, 7$), excited at 485 nm. The intensity of the excitation peaks of Pr$^{3+}$ $^{3}H_{4} \rightarrow ^{3}P_{0}$ transition and the R-lines of Cr$^{3+}$ both increase with increasing Pr$^{3+}$ concentration at fixed Cr$^{3+}$ concentration. The results indicate the occurrence of energy transfer from Pr$^{3+}$ $^{3}P_{0}$ state to Cr$^{3+}$.

Fig. 4 depicts the emission spectra of Cr$^{3+}$ in SAO: 1%Pr, $x\%$Cr ($x = 0, 1, 2, 3, 4$), excited into the $^{3}P_{2}$ state of Pr$^{3+}$ at 445 nm. The vertical lines represent the excitation states energies of Pr$^{3+}$ as observed in SAO: Pr.
of spectral properties and the dynamical processes indicate that the energy transfer from Pr\(^{3+}\) \(^{3}P_0\) 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 \(^{1}S_0\rightarrow^{1}I_6\) transition decreases greatly with the increasing of Cr\(^{3+}\) concentration, which suggests that there is energy transfer from the Pr\(^{3+}\) \(^{1}S_0\) 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 \(^{3}P_2\) states are compared in Fig. 6. Because in case the cross-relaxation occurs, a difference in evolution of the \(^{3}P_0\) 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 Pr\(^{3+}\) \(^{1}S_0\) state to Cr\(^{3+}\). Direct energy transfer can only populate the higher states of Cr\(^{3+}\), while for cross-relaxation, it will feed the Pr\(^{3+}\)--\(^{3}P_0\) level except for the excited states of Cr\(^{3+}\). Under excitation into the \(^{3}P_2\) state of Pr\(^{3+}\) the cross-relaxation cannot occur, but the energy transfer from \(^{3}P_0\) state to Cr\(^{3+}\) will take place and the Cr\(^{3+}\)-concentration-dependent emission of \(^{3}P_0\) 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 \(^{1}S_0\rightarrow^{1}I_6\) transition. The depopulation of \(^{1}I_6\) is dominated by multiphonon relaxation, i.e., all the electrons from \(^{1}S_0\) down to \(^{1}I_6\) will quickly relax to \(^{3}P_0\). The \(^{1}S_0\rightarrow^{1}I_6\) fluorescence intensity can be taken as a measure of the initial \(^{3}P_0\) population [5]. Thus, upon Pr\(^{3+}\) 4f5d excitation, when the intensities of \(^{1}S_0\rightarrow^{1}I_6\) transitions are normalized, the populations of the \(^{3}P_0\) 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 \(^{3}P_0\) states can be achieved by excitation into \(^{3}P_2\) states. The emissions of \(^{3}P_0\) states, excited into \(^{3}P_2\) states, have been shown in Fig. 6(b). The emission intensity of \(^{3}P_0\) state in SAO: 1\%Pr at 445 nm excitation has been scaled on the same emission upon 4f5d states excitation.
In conclusion, we have observed energy transfer from both \(^1\text{S}_0\) and \(^3\text{P}_0\) states of \(\text{Pr}^{3+}\) to \(\text{Cr}^{3+}\). Cross-relaxation process for \(\text{Pr}^{3+}–\text{Cr}^{3+}\) 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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