

Evidence for visible quantum cutting via energy transfer in SrAl₁₂O₁₉:Pr,Cr

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Evidence for visible quantum cutting involving the emission of two visible photons for each vacuum-ultraviolet (VUV) photon absorbed is demonstrated in SrAl₁₂O₁₉:Pr,Cr using synchrotron radiation as one of the excitation sources. Upon VUV excitation of the 4*f*5*d* states of Pr³⁺, quantum cutting could occur by a two-step energy transfer from Pr³⁺ to Cr³⁺ by cross relaxation and sequential transfer of the remaining excitation energy. A theoretical visible quantum efficiency of 147% is estimated in SrAl₁₂O₁₉:2% Pr,5% Cr, suggesting the possibility of a VUV phosphor with visible quantum efficiency higher than 100% based on Pr³⁺-Cr³⁺ pair in oxide materials. © 2007 Optical Society of America
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Crystals doped with rare-earth or transition metal ions are promising photonic sources for applications in optoelectronic devices such as lasers and displays. Recently, much interest has been paid to the development of highly efficient vacuum-ultraviolet (VUV)-excited phosphors in applications in such as plasma displays and mercury-free fluorescent tubes. In these devices, the phosphors that are currently used convert one VUV photon from the noble gas discharge into one visible photon and more than 50% of the absorbed energy losses. Therefore visible quantum-cutting (QC) phosphors, which can emit two visible photons for one VUV photon absorbed, have attracted considerable attention.¹ QC was first observed in some Pr³⁺-activated fluorides.² In general, when Pr³⁺ is excited to its 4*f*5*d* states, QC through a cascade emission due to ¹S₀-¹I₆ followed by ³P₀-³H₄ radiative transition could occur in some Pr³⁺-doped hosts in which the ¹S₀ level is located below the lowest 4*f*5*d* state.² However, such Pr³⁺-based QC phosphors have been found unsuitable for practical applications because the first-step transition, ¹S₀-¹I₆ about 402 nm, is near the UV region. An appropriate codopant that can convert this first-step photon to a proper visible photon through energy transfer (ET) could be a solution for this situation, but to our knowledge few results have been reported, especially in oxide materials.³

In this Letter visible QC via a two-step ET in SrAl₁₂O₁₉ (SAO):Pr,Cr was investigated. Cascade emission has been observed in SAO:Pr.⁴ Cr³⁺ is chosen because it has abundant absorption transitions

in SAO to match the Pr³⁺ ¹S₀ emissions, resulting in ET and red emission lines.

SAO:Pr, SAO:Cr, and SAO:Pr,Cr phosphors were prepared by solid-state reaction. The samples of SAO:2% Pr,*x*% Cr (mol ratio, *x*=1,2,3,5,7) were prepared. The VUV excitation spectra were measured at the VUV station at the National Synchrotron Radiation Laboratory (China) and were corrected using the excitation spectrum of sodium salicylate as a standard. The fluorescence spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer. The emission spectra were corrected for the response of the detector. For lifetime measurements, an optical parametric oscillator was used as the excitation source, and the signal was de-

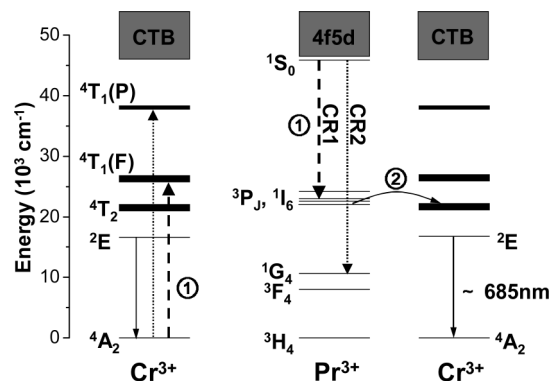


Fig. 1. Part of the energy-level scheme of Pr³⁺ and Cr³⁺ in SAO, showing the possibility of QC via a two-step ET from Pr³⁺ to Cr³⁺.

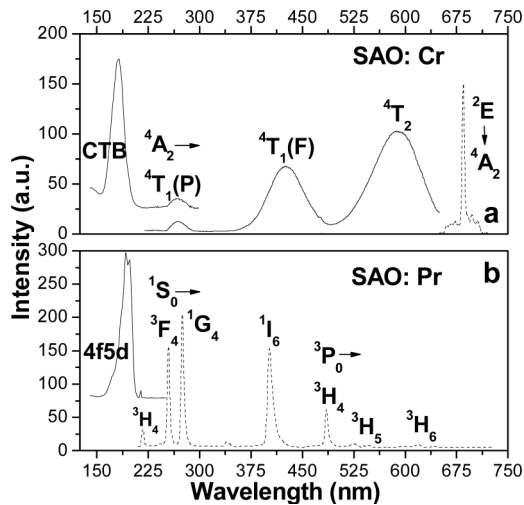


Fig. 2. a, VUV and UV excitation spectra (solid) of the Cr^{3+} 685 nm emission (dashed) in SAO:Cr. (b) VUV excitation spectrum (solid) of Pr^{3+} 402 nm emission and emission spectrum (dashed) upon 205 nm excitation in SAO:Pr.

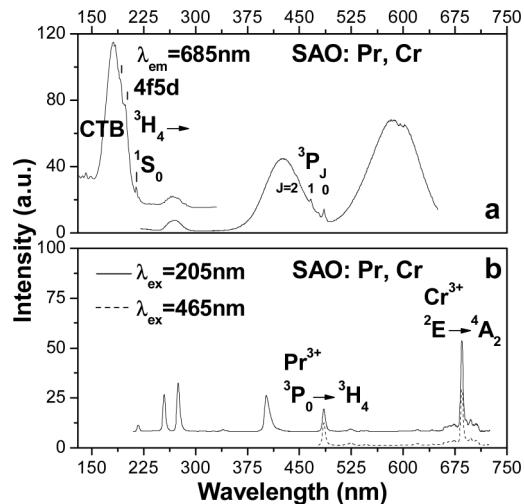


Fig. 3. a, VUV and UV excitation spectra of the Cr^{3+} 685 nm emission in SAO:Pr,Cr. b, Emission spectra of SAO:Pr,Cr upon 205 nm excitation (solid) and under 465 nm excitation (dashed). Two emission spectra are scaled to the 3P_0 emission intensities.

ected with a Tektronix digital oscilloscope (TDS 3052).

An energy-level diagram for the Pr^{3+} – Cr^{3+} pair, showing the possibility of QC via a two-step ET, is presented in Fig. 1. Upon excitation to the $4f5d$ states of a Pr^{3+} , first, part of the excitation energy is transferred to a Cr^{3+} by cross relaxations (CRs, CR1, and CR2 in Fig. 1), leading to Cr^{3+} in ${}^4T_1(F)$ or ${}^4T_1(P)$ excited states and the Pr^{3+} in 1I_6 or 1G_4 levels. Second, the populations quickly relax from 1I_6 down to 3P_0 ,⁵ where the remaining excitation is transferred to another Cr^{3+} . Consequently, the two-step ET results in two Cr^{3+} ions in excited states, and thereby finally converting a VUV photon absorbed by a Pr^{3+} into two red photons originating from 2E – 4A_2 transitions of two Cr^{3+} ions. It should be noted that the CRs in the first step depopulate the Pr^{3+} 1S_0 state but simulta-

neously populate the 1I_6 and 1G_4 states of Pr^{3+} . Thus an increase of the relative emission intensity of 3P_0 or 1G_4 relative to that of 1S_0 is expected in SAO:Pr,Cr compared with that in SAO:Pr if CR occurs. The occurrence of CR can therefore be evaluated by comparing the emission spectra upon Pr^{3+} $4f5d$ excitation in the samples with and without Cr^{3+} codoping.

The excitation and emission spectra of SAO:Pr and SAO:Cr are presented in Fig. 2. The emission of SAO:Cr consists of a 2E – 4A_2 zero-phonon line peaking at 685 nm and vibronic sidebands.⁶ The broad excitation around 180 nm is O^{2-} – Cr^{3+} related charge transfer band (CTB). Upon $4f5d$ excitation at 205 nm, the transitions of 1S_0 – 1I_6 and 3P_0 – 3H_4 constitute the cascade emission process.⁴ The bands in the VUV excitation spectrum are the absorptions of Pr^{3+} $4f5d$ states. The Pr^{3+} emissions of 1S_0 – 1I_6 at 402 nm, 1S_0 – 1G_4 at 273 nm, and 3P_0 – 3H_4 at 485 nm overlap Cr^{3+} excitations of 4A_2 – ${}^4T_1(F)$ and 4A_2 – ${}^4T_1(P)$ and also 4A_2 – ${}^4T_1(F)$ states, respectively. ET from Pr^{3+} 1S_0 and 3P_0 states to Cr^{3+} is possible under this condition.⁷

The excitation spectra of the Cr^{3+} 685 nm emission in SAO:2% Pr,5% Cr (SAO:Pr,Cr) are shown in Fig. 3(a). The Pr^{3+} 3H_4 – 3P_0 , 3P_1 , 3P_2 , 1S_0 transitions and the absorption of Pr^{3+} $4f5d$ bands, located on the right shoulder of O^{2-} – Cr^{3+} related CTB, all appear in the excitation spectra, implying that Cr^{3+} could be excited through the ET from Pr^{3+} 1S_0 and 3P_J to Cr^{3+} . In Fig. 3(b) the emission spectra upon 205 nm excitation and under 3P_1 excitation at 465 nm for SAO:Pr,Cr are displayed, respectively.

The emission spectra of Pr^{3+} in SAO:2% Pr, x % Cr ($x=0,1,2,3,5$) upon 205 nm excitation and under 465 nm excitation are displayed in Fig. 4. In the inset the emission spectra upon 205 nm excitation are normalized by the 1S_0 – 1I_6 emission intensity. First, the emission intensities of 1S_0 and 3P_0 at two different excitations both decrease with increasing x , which are consistent with the occurrence of ET from the Pr^{3+} 1S_0 and 3P_0 states to Cr^{3+} , respectively. Second,

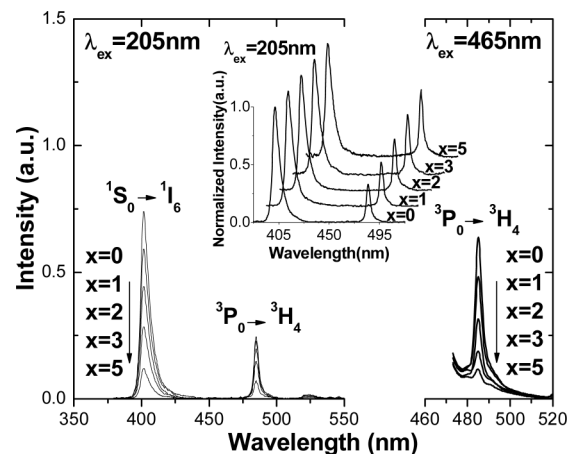


Fig. 4. Emission spectra of Pr^{3+} in SAO:2%Pr, x % Cr upon 205 nm excitation (left) and under 465 nm excitation (right). Inset, Normalized emission spectra of Pr^{3+} upon 205 nm excitation.

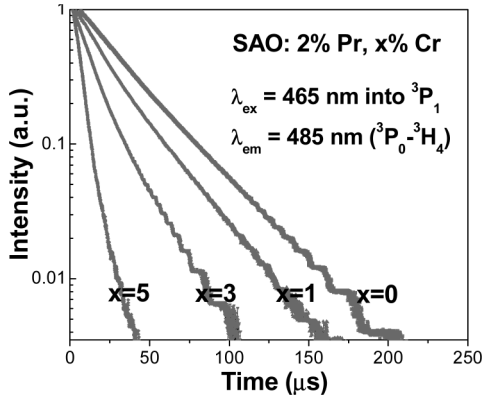


Fig. 5. Fluorescence decay curves of the $\text{Pr}^{3+}{}^3P_0$ emission in SAO:2%Pr, $x\%$ Cr under 465 nm excitation.

the expected increase in the relative emission intensity of 3P_0 to 1S_0 is observed as x increases upon 205 nm excitation (see inset), though the ET from 3P_0 to Cr^{3+} can simultaneously depopulate the 3P_0 level, resulting in decreasing relative intensity. This observation is consistent with the occurrence of CR1 in the ET from $\text{Pr}^{3+}{}^1S_0$ to Cr^{3+} .

The decay curves of the $\text{Pr}^{3+}{}^3P_0$ emission in SAO:2%Pr, $x\%$ Cr ($x=0,1,3,5$) under 465 nm excitation are plotted in Fig. 5. As x increases, the decay becomes faster and faster, which also suggests the occurrence of ET from 3P_0 to Cr^{3+} . From the decay curves, the efficiency of the second-step transfer can be determined by the equation $\eta_{\text{ET2}}=1-\tau/\tau_0$,⁸ where τ and τ_0 ($\sim 35\ \mu\text{s}$) are the decay times of the 3P_0 state with and without Cr^{3+} doping, respectively; $x=5$, $\tau \approx 7.3\ \mu\text{s}$, and η_{ET2} is $\sim 79\%$.

In continuous excitation upon the $4f5d$ states of Pr^{3+} , the populations of the 1S_0 (n_S) and 3P_0 (n_P) states satisfy the equation $[\gamma({}^1S_0-{}^1I_6)+W_{\text{CR1}}]n_S=n_P/\tau$, where $\gamma({}^1S_0-{}^1I_6)$ and W_{CR1} are the rates of ${}^1S_0-{}^1I_6$ transition and CR1, respectively. If R is the emission intensity ratio of ${}^3P_0-{}^3H_4$ to ${}^1S_0-{}^1I_6$, one has

$$W_{\text{CR1}}/\gamma({}^1S_0-{}^1I_6)=R\tau_0/R_0\tau-1. \quad (1)$$

We assume that there are no losses so that all energy either stays with Pr^{3+} or goes to Cr^{3+} in all cases, yielding a photon. The sum of the ET rates from $\text{Pr}^{3+}{}^1S_0$ to Cr^{3+} , W_{Sum} , can be estimated based on the intensity decrease of the 1S_0 emissions with x increases as shown in Fig. 4. Then one has

$$W_{\text{Sum}}/\gamma({}^1S_0-{}^1I_6)=[I({}^1S_0-{}^6I_6)_0/I({}^1S_0-{}^6I_6)_x-1]/\alpha, \quad (2)$$

where $\alpha=0.39$ is the branching ratio of ${}^1S_0-{}^1I_6$ transition to all 1S_0 transitions, which can be obtained

from the emission spectrum in Fig. 2(b), and $I({}^1S_0-{}^1I_6)_x$ and $I({}^1S_0-{}^1I_6)_0$ are the emission intensities of the ${}^1S_0-{}^1I_6$ transition for x and $x=0$, respectively. The ET quantum efficiency (QE) from $\text{Pr}^{3+}{}^1S_0$ to Cr^{3+} , η_{CR1} for CR1 and η_{Sum} for overall, can be expressed as

$$\eta_{\text{CR1}}=W_{\text{CR1}}/[W_{\text{Sum}}+\gamma({}^1S_0-{}^1I_6)/\alpha], \quad (3)$$

$$\eta_{\text{Sum}}=W_{\text{Sum}}/[W_{\text{Sum}}+\gamma({}^1S_0-{}^1I_6)/\alpha]. \quad (4)$$

If we take the blue ${}^3P_0-{}^3H_4$ emission into account, the visible QE of QC, η_{QC} , can be determined using the following equation:

$$\eta_{\text{QC}}=\eta_{\text{Sum}}+[\eta_{\text{CR1}}+(1-\eta_{\text{Sum}})\alpha][\eta_{\text{ET2}}+(1-\eta_{\text{ET2}})\beta], \quad (5)$$

where $\beta=0.42$ is the branching ratio of the ${}^3P_0-{}^3H_4$ transition to all 3P_0 transitions.⁵ Using Eqs. (1)–(5), η_{CR1} , η_{Sum} , and η_{QC} can be evaluated. $\eta_{\text{CR1}}=69\%$, $\eta_{\text{Sum}}=82\%$, and $\eta_{\text{QC}}=147\%$ are obtained for $x=5$.

In summary, evidence for QC via a two-step ET from Pr^{3+} to Cr^{3+} was observed in SAO:Pr,Cr. A theoretical internal visible QE of 147% is possible in SAO:2%Pr,5%Cr, exhibiting the feasibility of achieving a VUV phosphor with QE greater than unity based on the $\text{Pr}^{3+}-\text{Cr}^{3+}$ pair. The mechanism of this transfer needs to be further studied.

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