Evidence for visible quantum cutting via energy transfer in \( \text{SrAl}_{12}\text{O}_{19}:\text{Pr},\text{Cr} \)

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Received December 5, 2006; revised January 18, 2007; accepted January 23, 2007; posted January 29, 2007 (Doc. ID 77771); published March 19, 2007

Evidence for visible quantum cutting involving the emission of two visible photons for each vacuum-ultraviolet (VUV) photon absorbed is demonstrated in \( \text{SrAl}_{12}\text{O}_{19}:\text{Pr},\text{Cr} \) using synchrotron radiation as one of the excitation sources. Upon VUV excitation of the \( 4f^55d \) states of \( \text{Pr}^{3+} \), quantum cutting could occur by a two-step energy transfer from \( \text{Pr}^{3+} \) to \( \text{Cr}^{3+} \) by cross relaxation and sequential transfer of the remaining excitation energy. A theoretical visible quantum efficiency of 147% is estimated in \( \text{SrAl}_{12}\text{O}_{19}:2\% \text{ Pr},5\% \text{ Cr} \), suggesting the possibility of a VUV phosphor with visible quantum efficiency higher than 100% based on \( \text{Pr}^{3+}–\text{Cr}^{3+} \) pair in oxide materials. © 2007 Optical Society of America

OCIS codes: 160.2540, 300.2530.

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 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 \( \text{Pr}^{3+} \)-activated fluorides.\(^2\) In general, when \( \text{Pr}^{3+} \) is excited to its \( 4f5d \) states, QC through a cascade emission due to \( 1S_0–1I_6 \) followed by \( 3P_0–3H_4 \) radiative transition could occur in some \( \text{Pr}^{3+} \)-doped hosts in which the \( 1S_0 \) level is located below the lowest \( 4f5d \) state.\(^2\) However, such \( \text{Pr}^{3+} \)-based QC phosphors have been found unsuitable for practical applications because the first-step transition, \( 1S_0–1I_6 \) 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 \( \text{SrAl}_{12}\text{O}_{19} \) (SAO):\( \text{Pr},\text{Cr} \) was investigated. Cascade emission has been observed in SAO:Pr.\(^4\) \( \text{Cr}^{3+} \) is chosen because it has abundant absorption transitions in SAO to match the \( \text{Pr}^{3+}1S_0 \) 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% \( \text{Pr},x\% \text{ Cr} \) (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 \( \text{Pr}^{3+} \) and \( \text{Cr}^{3+} \) in SAO, showing the possibility of QC via a two-step ET from \( \text{Pr}^{3+} \) to \( \text{Cr}^{3+} \).](image-url)
tected 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 $^3P_0$ 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$$^g$$^-$A$_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 simultane-

ously 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 $^4E$$^g$$^-$A$_2$ zero-phonon line peaking at 685 nm and vibronic sidebands. The broad excitation around 180 nm is O$^{2-}$$^-$Cr$^{3+}$ related charge transfer band (CTB). Upon 4f5d excitation at 205 nm, the transitions of $^1S_0$$^-$$^1I_6$ and $^3P_0$$^-$$^3H_4$ constitute the cascade emission process. The bands in the VUV excitation spectrum are the absorptions of Pr$^{3+}$ 4f5d states. The Pr$^{3+}$ emissions of $^1S_0$$^-$$^1I_6$ at 402 nm, $^1S_0$$^-$$^1G_4$ at 273 nm, and $^3P_0$$^-$$^3H_4$ at 485 nm overlap Cr$^{3+}$ excitations of $^4A_2$$^g$$^-$$^4T_{1}(F)$ and $^4A_2$$^g$$^-$$^4T_{1}(P)$ and also $^4A_2$$^g$$^-$$^4T_{1}(F)$ states, respectively. ET from Pr$^{3+}$ $^1S_0$ and $^3P_0$ states to Cr$^{3+}$ is possible under this condition.

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 $^3P_0$ states 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,
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 \(Pr^{3+}1S_0\) to \(Cr^{3+}\).

The decay curves of the \(Pr^{3+}3P_0\) 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 \(\eta_{ET2}=1-\tau/\tau_0\) where \(\tau\) and \(\tau_0\) \((-35\mu s)\) are the decay times of the \(3P_0\) state with and without \(Cr^{3+}\) doping, respectively; \(x=5, \tau=7.3\mu s\), and \(\eta_{ET2}\) is -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 \(\gamma(1S_0^{-1}I_6)+W_{CR1}n_S=n_p/\tau\), where \(\gamma(1S_0^{-1}I_6)\) and \(W_{CR1}\) are the rates of \(1S_0^{-1}I_6\) transition and CR1, respectively. If \(R\) is the emission intensity ratio of \(3P_0^{-1}H_4\) to \(1S_0^{-1}I_6\), one has

\[
W_{CR1}/\gamma(1S_0^{-1}I_6) = R\tau/\tau_0 \tau - 1.
\]

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 \(Pr^{3+}1S_0\) 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

\[
W_{Sum}/\gamma(1S_0^{-1}I_6) = [I(1S_0^{-6}I_6)/I(1S_0^{-6}I_6)] - 1/\alpha,
\]

where \(\alpha=0.39\) is the branching ratio of \(1S_0^{-1}I_6\) transition to all \(1S_0\) transitions, which can be obtained from the emission spectrum in Fig. 2(b), and \(I(1S_0^{-6}I_6)\) and \(I(1S_0^{-6}I_6)\) are the emission intensities of the \(1S_0^{-1}I_6\) transition for \(x\) and \(x=0\), respectively. The ET quantum efficiency (QE) from \(Pr^{3+}\) to \(Cr^{3+}\), \(\eta_{CR1}\) for CR1 and \(\eta_{Sum}\) for overall, can be expressed as

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

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

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

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

where \(\beta=0.42\) is the branching ratio of the \(3P_0^{-3}H_4\) transition to all \(3P_0\) transitions. Using Eqs. (1)–(5), \(\eta_{CR1}\), \(\eta_{Sum}\), and \(\eta_{QC}\) can be evaluated. \(\eta_{CR1}=69\%\), \(\eta_{Sum}=82\%\), and \(\eta_{QC}=147\%\) 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 \(Pr^{3+}–Cr^{3+}\) pair. The mechanism of this transfer needs to be further studied.

This work is supported by MOST of China (2006CB601104, 2006AA03A138), the National Science Foundation of China (10574128, 10504031) and by the Cotrell College Science Awards from Research Corporation. E-mail addresses are, J. Zhang, zhangjh@ciomp.ac.cn; X. Wang, xwang@georgiasouthern.edu.

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