

Investigation of Pr^{3+} as a sensitizer in quantum-cutting fluoride phosphorsTe-Ju Lee,^{1,2} Li-Yang Luo,¹ Bing-Ming Cheng,² Wei-Guang Diao,¹ and Teng-Ming Chen^{1,a)}¹Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan²National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

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A quantum-cutting (QC) phosphor $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}$ shows poor optical absorption and a theoretical quantum efficiency (QE) of 107% in the ultraviolet (UV) and vacuum ultraviolet (VUV) excitation spectral ranges. Pr^{3+} was codoped as a sensitizer in $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}$, thus increasing the absorption in the UV and VUV spectral regions; the theoretical QE of $\text{K}_2\text{GdF}_5:\text{Eu}^{3+},\text{Pr}^{3+}$ was increased to 138%. The spectra indicate that the possible mechanisms of QC and energy transfer differ from those of phosphors containing the $\text{Gd}^{3+}-\text{Eu}^{3+}$ couple. Temporally resolved measurements of fluorescence decay confirm the proposed QC mechanism for the phosphor containing the $\text{Gd}^{3+}-\text{Eu}^{3+},\text{Pr}^{3+}$ system. © 2008 American Institute of Physics. [DOI: 10.1063/1.2884690]

High-performance mercury-free lighting and plasma display panels (PDP), which are generally excited with a xenon dimer discharge in broadbands about 147 and 172 nm, rely critically on phosphors that should have great efficiency of luminescence in the vacuum ultraviolet (VUV) region. Most known phosphors still suffer from a poor quantum efficiency (QE) relative to those used in fluorescent lamps or cathode-ray tubes found in color television sets. To remedy this deficiency, one strategy involves use of one UV or VUV photon to excite the phosphor, thus, to obtain more than one visible emitted photon; this phenomenon is called a quantum-cutting (QC) effect.

Quantum cutting was reported in $\text{YF}_3:\text{Pr}^{3+}$ in 1974, but there exists no efficient quantum cutter in the visible spectral region.^{1,2} Wegh *et al.*³ reported the observation of visible QC by down conversion in the $\text{LiGdF}_4:\text{Eu}^{3+}$ that exhibited a theoretical, rather than empirical QE as great as 198%. Vergeer *et al.*⁴ reported recently that Pr^{3+} acts as a sensitizer, wherein the luminescence of Pr^{3+} was quenched by Eu^{3+} . Here, we report photoluminescence (PL) and PL excitation (PLE) spectra of $\text{K}_2\text{GdF}_5:\text{Eu}^{3+},\text{Pr}^{3+}$ and relevant transient decay behavior of this phosphor; we propose a mechanism of down conversion and energy transfer (ET) to rationalize the observed visible QC effect.

Samples of $\text{K}_2\text{GdF}_5:\text{Eu}^{3+},\text{Pr}^{3+}$ (5%, $x\%$) in a series with $x=0, 0.1, 0.5, 1, 1.5,$ and 2 as varied Pr^{3+} contents were prepared on reacting KF (Acros, 99%), GdF_3 (Aldrich, 99.99%), EuF_3 (Strem, 99.99%), and PrF_3 (Aldrich, 99.99%) in stoichiometric proportions in an evacuated and sealed silica tube at 600 °C for 8 h. The samples were then examined by x-ray diffraction (Bruker AXS D8 advanced automatic diffractometer). The PL spectra of phosphors were measured with a synchrotron as excitation source; the emission was analyzed with a 0.32 m monochromator and detected with a photomultiplier in a photon-counting mode. The VUV source was the high-flux beamline attached to the 1.5 GeV storage ring at the National Synchrotron Radiation Research Center, Taiwan. Temporally resolved decays of the emission were performed with a tunable nanosecond optical-parametric-oscillator/Q-switch-pumped Nd:yttrium aluminum garnet laser system. Emission transients were collected

with a monochromator, detected with a photomultiplier tube connected to a digital oscilloscope, and transferred to a computer for kinetics analysis.⁵ The empirical QE was measured by using a Jobin Yvon-Spex Fluorolog 3 spectrofluorometer equipped with a model FL-PLQY integrating sphere.

For a practical calculation of the extra QE resulting from cross relaxation, some essential premises must be stated. For instance, VUV-UV absorption by phosphors is disregarded; possible nonradiative losses due to energy migration at defects and impurities in the samples are ignored. The QE of $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}$ (5%), exhibiting a QC mechanism, is consistent with that of $\text{LiGdF}_4:\text{Eu}^{3+}$ containing the $\text{Gd}^{3+}-\text{Eu}^{3+}$ couple reported previously,³ which was found to be 107%. The samples with Pr^{3+} in varied proportions doped as a sensitizer into $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}$ with the $\text{Gd}^{3+}-\text{Eu}^{3+}$ couple were prepared. In the PLE spectrum shown in Fig. 1, two broad absorption bands of Pr^{3+} are centered at 172 and 210 nm when monitored at 588 ($^5D_0 \rightarrow ^7F_1$) and 509 nm ($^5D_2 \rightarrow ^7F_3$), respectively. Two broadbands due to $\text{K}_2\text{GdF}_5:5\% \text{Eu}^{3+}, 1\% \text{Pr}^{3+}$ are attributed to $f-d$ transitions of Pr^{3+} .^{6,7} The transitions are from the $\text{Pr}^{3+} ^3H(4f)$ ground state to the spin-allowed excited state $^3H(4f5d)$. The absorptions centered at 165 nm or shorter wavelength might be due to a

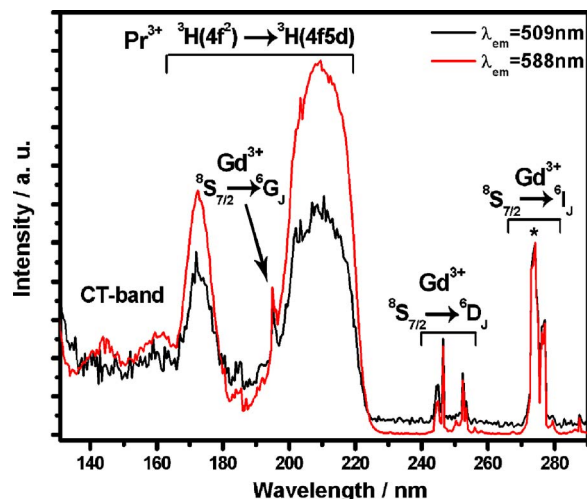


FIG. 1. (Color online) PLE spectra of $\text{K}_2\text{GdF}_5:\text{Eu}^{3+},\text{Pr}^{3+}$ monitored at $\lambda_{\text{em}}=509$ and 588 nm. The spectra were scaled to the $^8S_{7/2} \rightarrow ^6I_J$ excitation intensity (*).

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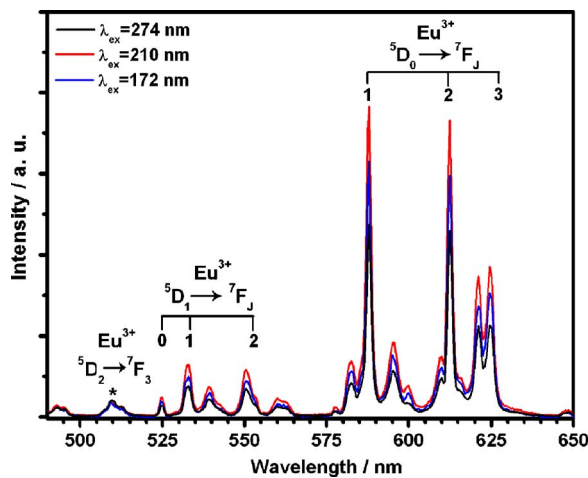


FIG. 2. (Color online) Comparison of PL spectra for $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$ with $\lambda_{\text{ex}}=274$ nm (no QC effect), 210 nm, and 172 nm (showing QC effect). The spectra were scaled to the ${}^5D_2 \rightarrow {}^7F_3$ at 509 nm excitation intensity (*).

charge-transfer (CT) transition. The excitation attributed to ${}^8S_{7/2} \rightarrow {}^6G_J$ of Gd^{3+} centered at 195 nm was observed almost to overlap the Pr^{3+} absorption band.

Figure 2 compares the PL spectra for $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$ phosphors at three excitation wavelengths (λ_{ex})—274, 210, and 172 nm. The intensity of ${}^5D_1 \rightarrow {}^7F_j$ and ${}^5D_0 \rightarrow {}^7F_j$ emissions attributed to the Eu^{3+} multiplet transition was observed to become significantly more intense in the phosphor containing the $\text{Gd}^{3+}-\text{Eu}^{3+}-\text{Pr}^{3+}$ system, than for $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}$, when Pr^{3+} was doped and excited to the $4f5d$ state at 210 and 172 nm, respectively. A calculation of the theoretical QE $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$ (5%, $x\%$) ($x=0, 0.1, 0.5, 1, 1.5$, and 2) phosphors was based on an equation suggested by Wegh *et al.*³ and later modified by Lee *et al.*⁸ The theoretical QE was found to increase from 107% for $\text{K}_2\text{GdF}_5:5\% \text{Eu}^{3+}$ to an optimal value 138% for $\text{K}_2\text{GdF}_5:5\% \text{Eu}^{3+}, 1\% \text{Pr}^{3+}$ under excitation at 210 nm. This observation indicates that Pr^{3+} plays an important role in sensitizing Eu^{3+} and becomes quenched by neighboring Eu^{3+} ions to enhance the luminescence intensity through a QC effect.

Pr^{3+} showing an intrinsic absorption might thus act as an effective sensitizer for the phosphor system containing $\text{Gd}^{3+}-\text{Eu}^{3+}-\text{Pr}^{3+}$. The energy level diagrams depicted in Fig. 3 describe the possible mechanisms for QC and ET in the $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$ phosphors.^{9,10} Figure 3(a) indicates that under excitation at 274 nm, as soon as the Gd^{3+} ion is excited into the 6I_J state, following a nonradiative relaxation to the 6P_J state, direct ET might occur from 6P_J to neighboring Eu^{3+} ions, or a radiative relaxation of Gd^{3+} from 6P_J to the ${}^8S_{7/2}$ ground state occurs; consequently, no QC is expected, as indicated in the proposed diagram. In contrast, Fig. 3(b) indicates that under excitation at 210 nm, Pr^{3+} pumping dominates when Pr^{3+} is excited to the $4f5d$ state, as the energy released from transitions ${}^1S_0 \rightarrow {}^3P_1 + {}^1I_6$ matches and feeds the excitation transition ${}^7F_J \rightarrow {}^5D_3$; ET from Pr^{3+} to neighboring Eu^{3+} ions might proceed by cross relaxation (step ①), which can further induce emission of multiplet transitions ${}^5D_{0,1,2,3} \rightarrow {}^7F_J$ ($J=0-6$). The remaining energy in 3P_1 or 3P_0 of Pr^{3+} is subsequently transferred (step ②) directly to nearby Eu^{3+} ions, from which emissions attributed to transitions ${}^5D_{0,1} \rightarrow {}^7F_J$ ($J=0-6$) occur. This proposal is rationalized by considering that, after the nonradiative decay

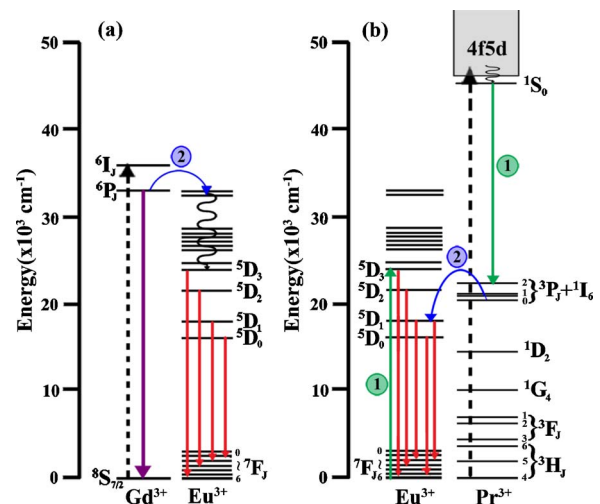


FIG. 3. (Color online) Schematic energy levels of $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$ showing possible mechanisms for visible QC with excitation in the VUV with $\lambda_{\text{ex}}=(\text{a})$ 274 and (b) 210 nm (① and ② denote the cross relaxation and direct energy transfer, respectively).

from 3P_1 to 3P_0 states, the remaining energy in the $\text{Pr}^{3+} {}^3P_0$ level is insufficient to transfer to levels 5D_2 or higher 5D_J of neighboring Eu^{3+} ions.¹¹ The mechanism of ET involved in this $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$ phosphor results in a QE of visible luminescence much increased over that observed in $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}$. The QE of $\text{K}_2\text{GdF}_5:5\% \text{Eu}^{3+}$ was calculated to be 107%, but that for $\text{K}_2\text{GdF}_5:5\% \text{Eu}^{3+}, 1\% \text{Pr}^{3+}$ is 138%.⁸ Table I shows the dependence of Pr^{3+} content on the QE in the visible region of the $\text{K}_2\text{GdF}_5:5\% \text{Eu}^{3+}, x\% \text{Pr}^{3+}$ phosphors. The codoping of Pr^{3+} was demonstrated to increase the QE of $\text{K}_2\text{GdF}_5:5\% \text{Eu}^{3+}, x\% \text{Pr}^{3+}$. The greatest QE attained with excitation at 210 nm was found to be 138% for the sample codoped with 1% Pr^{3+} . For phosphors with proportions of Pr^{3+} dopant greater than 1%, a large fraction of energy feeds the ${}^1S_0 \rightarrow {}^3P_2$ emission, and the loss of a small fraction of ET is considered to be responsible for the observed decrease of QE. When $\text{K}_2\text{GdF}_5:5\% \text{Eu}^{3+}, x\% \text{Pr}^{3+}$ phosphors were excited at 172 nm, the trend of QE versus x indicated in Table I was similar to that observed with 210 nm as the excitation wavelength.

We also measured the time-resolved PL spectra of $\text{K}_2\text{GdF}_5:5\% \text{Eu}^{3+}, 1\% \text{Pr}^{3+}$ by monitoring the Eu^{3+} ion at the 5D_1 and 5D_0 states upon excitation of Pr^{3+} at the $4f5d$ state ($\lambda_{\text{ex}}=215$ nm). Figure 4 shows the corresponding decay curves, which were fitted according to a consecutive kinetic model, $A \rightarrow B \rightarrow C \rightarrow D$. In this model, the $A \rightarrow B$ process corresponds to the cross relaxation between the ${}^1S_0 \rightarrow {}^3P_J$ transition of Pr^{3+} and the ${}^7F_J \rightarrow {}^5D_3$ transition of Eu^{3+} ; the $B \rightarrow C$ process corresponds to the energy transfer and the

TABLE I. Variation of QE for $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$ (5%, $x\%$) as a function of Pr^{3+} content (x) with excitation at 210 and 172 nm.

x	Quantum efficiency (%)	
	$\lambda_{\text{ex}}(\text{nm})=210$	172
0.1	106	111
0.5	120	133
1.0	123	138
1.5	119	134
2.0	116	131

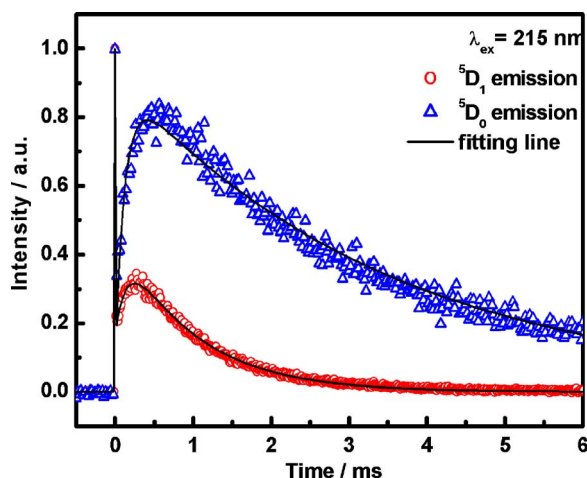


FIG. 4. (Color online) Temporally resolved decay curves of 5D_1 (533 nm) and 5D_0 (588 nm) emissions with excitation into $\text{Pr}^{3+} {}^1S_0$ for $\text{K}_2\text{GdF}_5:5\% \text{Eu}^{3+}, 1\% \text{Pr}^{3+}$. Solid lines are fitted with a multiexponential decay.

relaxation of 5D_J state ($J \geq 2$); the $C \rightarrow D$ process corresponds to the relaxation of the 5D_1 or the 5D_0 state of Eu^{3+} . Our time-dependent results indicate that the spike signals represent the rapid cross relaxation ($< 3 \mu\text{s}$) corresponding to the $\text{Pr}^{3+}, {}^1S_0 \rightarrow {}^3P_1$ down transition together with the $\text{Eu}^{3+}, {}^7F_7 \rightarrow {}^5D_3$ up transition. Therefore, the populations in the 5D_1 and the 5D_0 states of Eu^{3+} were enhanced by two contributions—one is due to the fast relaxation of the $\text{Eu}^{3+} {}^5D_3$ state itself and the other is due to the interionic energy transfer from the $\text{Pr}^{3+} {}^3P_J$ states into the 5D_1 state of Eu^{3+} . Both relaxation and ET processes take $\sim 0.13 \text{ ms}$, which is responsible for the rising part of the transients. The observed 0.96 and 3.52 ms decays of the transients represent the radiative and the nonradiative relaxations of the 5D_1 and the 5D_0 states, respectively. Our time-dependent results are fully consistent with the mechanistic scheme given in Fig. 3(b), and the results are also similar to those of Vergeer *et al.* for the $\text{LiGdF}_4:\text{Eu}^{3+}$ system excited at the 6G_J state of Gd^{3+} .¹²

To gain a realistic sense of luminescence efficiency, we have determined the empirical QE of $\text{K}_2\text{GdF}_5:5\% \text{Eu}^{3+}, 1\% \text{Pr}^{3+}$ to be 93% when excited at 274 nm (no QC effect) by using an integrating sphere. However, QE under excitation at 210 or 172 nm (with QC effect) can be inferred semiempirically and found to be 180% and 118%, respectively, by considering the proportionality of the observed PL intensity enhancement revealed in Fig. 2 and using 93% (without QC effect) as a basis since the direct determination of QE is not feasible in our laboratory.

In conclusion, we have demonstrated that $\text{K}_2\text{GdF}_5:5\% \text{Eu}^{3+}, x\% \text{Pr}^{3+}$ are red-emitting QC phosphors of which the theoretical QE was improved from 107% to 138% on codoping Pr^{3+} as a sensitizer through mechanisms of cross relaxation and direct energy transfer. According to a comparison of the $\text{Gd}^{3+}-\text{Eu}^{3+}$ couple and the $\text{Gd}^{3+}-\text{Eu}^{3+}-\text{Pr}^{3+}$ system, Pr^{3+} ion shows intrinsically effective absorption in the UV and VUV spectral ranges, and exhibits a prospectively improved efficiency of phosphors used in PDP and mercury-free lamps that are excited with the Xe_2 discharge.

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