

# Investigation of $\text{Pr}^{3+}$ as a Sensitizer in Quantum-cutting Fluoride Phosphors

A red-emitting quantum-cutting (QC) phosphor  $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}$  shows poor optical absorption and a theoretical quantum efficiency (QE) 107 % in the ultraviolet (UV) and vacuum ultraviolet (VUV) excitation spectral ranges.  $\text{Pr}^{3+}$  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 improved to reach 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.

Most phosphors reported to date still suffer from a poor quantum efficiency (QE) relative to those used in fluorescent lamps or cathode-ray tubes. To remedy this deficiency, one strategy involves use of one ultraviolet (UV) or vacuum ultraviolet (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 first reported in  $\text{YF}_3:\text{Pr}^{3+}$  in 1974, but there exists no efficient quantum cutter in the visible spectral region. Wegh *et al.* reported in 1999 the observation of visible quantum cutting by down conversion in the  $\text{LiGdF}_4:\text{Eu}^{3+}$  phosphor that exhibited a theoretical, rather than empirical, quantum efficiency (QE) as great as 198 %. Vergeer *et al.* reported recently that  $\text{Pr}^{3+}$  acts as a sensitizer, wherein the luminescence of  $\text{Pr}^{3+}$  was quenched by  $\text{Eu}^{3+}$ . Here we report results on the red-emitting  $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$  phosphor from our investigation of the UV and VUV excitation, emission spectra, and the relevant transient decay behavior of this phosphor; we propose a mechanism of down conversion and energy transfer to rationalize the observed visible quantum-cutting effect.

Samples with composition  $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$  (5 %,  $x$  %) in a series with  $x = 0, 0.1, 0.5, 1, 1.5, 2$  as varied  $\text{Pr}^{3+}$  content were prepared and characterized according to those reported by Lee *et al.* The VUV source used was the high-flux beamline attached to the 1.5-GeV storage ring provided by the National Synchrotron Radiation Research Center in Hsinchu, Taiwan.

Wegh *et al.* reported the QC and energy transfer in a  $\text{LiGdF}_4:\text{Eu}^{3+}$  phosphor system with optimal QE of 198%, in which  $\text{Gd}^{3+}$  ion served as the quantum cutter and  $\text{Eu}^{3+}$  ion as the activator. For a practical calculation of the extra QE resulting from cross relaxation, some essential premises must be stated. For instance, VUV-UV absorption by

## ◎ Beamline

03A1 BM-High Flux VUV

## ◎ Authors

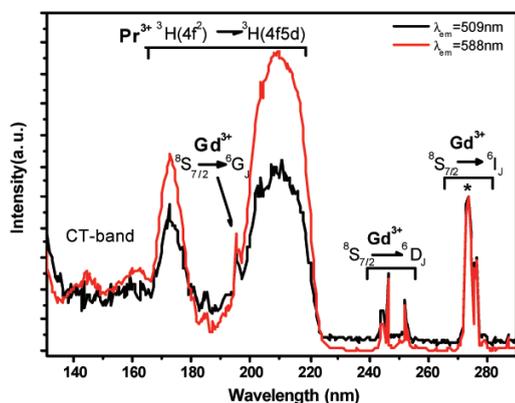
**T. -J. Lee and T. -M. Chen**

National Chiao Tung University, Hsinchu, Taiwan

**B. -M. Cheng**

National Synchrotron Radiation Research Center, Hsinchu, Taiwan





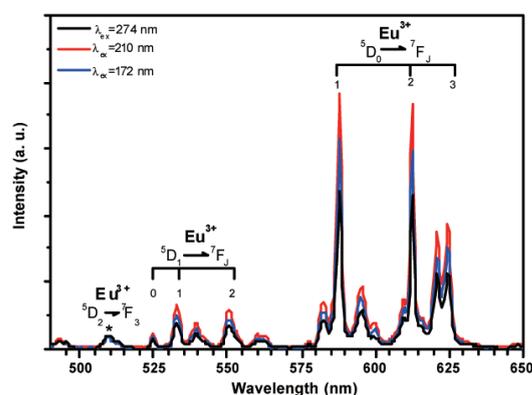
**Fig. 1:** PLE spectra of  $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$  monitored at  $\lambda_{\text{em}} = 509$  and  $588$  nm. The spectra were scaled to the  ${}^8\text{S}_{7/2} \rightarrow {}^6\text{I}_J$  excitation intensity (\*).

phosphors is disregarded; possible non-radiative losses due to energy migration at defects and impurities in the samples are ignored. Samples of  $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}$  with  $\text{Pr}^{3+}$  in varied proportion doped as a sensitizer were prepared; the PL and PLE spectra were investigated. In the PLE spectrum shown in Fig. 1, two broad absorption bands of  $\text{Pr}^{3+}$  are centered at 172 and 210 nm when monitored at 588 ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ) and 509 nm ( ${}^5\text{D}_2 \rightarrow {}^7\text{F}_3$ ), respectively. Two broad bands due to  $\text{K}_2\text{GdF}_5:5\%\text{Eu}^{3+}, 1\%\text{Pr}^{3+}$  are attributed to f-d transitions of  $\text{Pr}^{3+}$ . The transitions are from the  $\text{Pr}^{3+}$   ${}^3\text{H}(4f)$  ground state to the spin-allowed excited state  ${}^3\text{H}(4f5d)$ . The absorptions centered at 165 nm or shorter wavelength might be due to a charge-transfer (CT) transition. The excitation attributed to  ${}^8\text{S}_{7/2} \rightarrow {}^6\text{G}_J$  of  $\text{Gd}^{3+}$  centered at 195 nm was observed almost to overlap the  $\text{Pr}^{3+}$  absorption band.

Figure 2 compares PL spectra for  $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$  phosphors at three excitation wavelengths ( $\lambda_{\text{ex}}$ )-274 nm (showing no QC effect), 210 nm and 172 nm (both showing a QC effect). The spectra were scaled to the emission intensity of transition  ${}^5\text{D}_2 \rightarrow {}^7\text{F}_3$  at 509 nm. The PL intensity of  ${}^5\text{D}_1 \rightarrow {}^7\text{F}_J$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  emissions attributed to the  $\text{Eu}^{3+}$  multiplet transition were 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  $\text{Pr}^{3+}$  was doped and excited to the 4f5d state at 210 and 172 nm, respectively. A calculation of the theoretical QE for  $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}(5\%)$  and  $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}(5\%, x\%)$  ( $x = 0.1, 0.5, 1, 1.5, 2$ ) phosphors was based on an equation suggested by Wegh *et al.* and later modified by Lee *et al.* The theoretical QE was found to increase from 107 % for  $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}(5\%)$  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  $\text{Pr}^{3+}$  plays an important role to sensitize  $\text{Eu}^{3+}$  and becomes quenched by neighboring  $\text{Eu}^{3+}$  ions to enhance the luminescence intensity through a quantum-cutting effect.

$\text{Pr}^{3+}$  that shows an intrinsic absorption in the UV and VUV spectral ranges might thus act as an effective sensitizer for the phosphor system containing  $\text{Gd}^{3+}-\text{Eu}^{3+}-\text{Pr}^{3+}$ . The energy levels diagrams depicted in Fig. 3 describe the possible mechanisms for quantum cutting and energy transfer in the  $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$  phosphor system. Figure 3 (a) indicates that, under excitation at 274 nm, as soon as the  $\text{Gd}^{3+}$  ion is excited into the  ${}^6\text{I}_J$  state (indicated by a dashed arrow), following non-radiative relaxation to the  ${}^6\text{P}_J$  state, direct energy transfer might occur from  ${}^6\text{P}_J$  to neighboring  $\text{Eu}^{3+}$  ions, or some radiative relaxation of  $\text{Gd}^{3+}$



**Fig. 2:** 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  ${}^5\text{D}_2 \rightarrow {}^7\text{F}_3$  @509 nm excitation intensity (\*).

from  ${}^6P_J$  to the  ${}^8S_{7/2}$  ground state occurs; consequently, no quantum cutting is expected, as indicated in the proposed diagram. In contrast, Fig. 3(b) indicates that, under excitation at 210 nm,  $\text{Pr}^{3+}$  pumping dominates, when  $\text{Pr}^{3+}$  is excited to the 4f5d state (indicated by a dashed arrow), as the energy released from transitions  ${}^1S_0 \rightarrow {}^3P_1 + {}^1I_6$  matches and feeds the excitation transition  ${}^7F_J \rightarrow {}^5D_{3;}$ ; energy transfer from  $\text{Pr}^{3+}$  to neighboring  $\text{Eu}^{3+}$  ions might proceed by cross relaxation (step①), 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  $\text{Pr}^{3+}$  is subsequently transferred (step②) directly to nearby  $\text{Eu}^{3+}$  ions, from which emissions attributed to transitions  ${}^5D_{0,1} \rightarrow {}^7F_J (J = 0 - 6)$  occur. This proposal is rationalized on considering that, after the non-radiative decay 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  $\text{Eu}^{3+}$  ions. The mechanism of energy transfer 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  $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}(5\%)$  was calculated to be 107 % but for  $\text{K}_2\text{GdF}_5: 5\%\text{Eu}^{3+}, 1\%\text{Pr}^{3+}$  is 138 %. When

$\text{K}_2\text{GdF}_5: 5\%\text{Eu}^{3+}, x\%\text{Pr}^{3+}$  phosphors are excited at 172 nm, the mechanism of energy transfer and QC is expected to be similar to that at 210 nm as the excitation wavelength.

The theoretical QE of the red-emitting  $\text{K}_2\text{GdF}_5:\text{Eu}^{3+}, \text{Pr}^{3+}$  QC phosphor has been demonstrated to be improved from 107 % to 138 % on codoping  $\text{Pr}^{3+}$  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,  $\text{Pr}^{3+}$  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 dimer discharge. ◆

#### Experimental Station

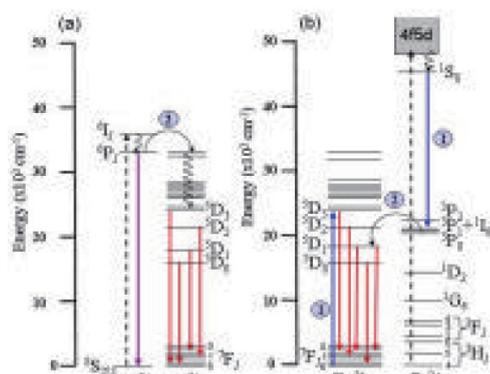
HF-CGM (Gas Phase/Photoluminescence)

#### Publication

T. -J. Lee, L. Luo, B. -M. Cheng, E. W. -G. Diau, and T. -M. Chen, Applied Physics Letters **92**, 081106-081108 (2008).

#### Contact E-mail

tmchen@mail.nctu.edu.tw



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