Investigation of Quantum Cutting in Non-Fluoride Green-Emitting Phosphors via Down-Conversion

Ya-Ting Tu (涂雅婷) and Teng-Ming Chen (陳登銘)

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan

The idea of quantum cutting (QC) is that a VUV photon or an ultraviolet (UV) photon with higher energy can be split into two visible photons. Despite this apparent limitation, it is theoretically possible to obtain visible emissions with 200% quantum efficiency (QE) of for the phosphor through the QC process. In this work, we report the QC phenomenon and propose a energy transfer mechanism in an unprecedented gadolinium oxyfluoride phosphor, $Gd_{4-x}Tb_xO_3F_6$ ($0 \leq x \leq 1.0$). The PL excitation spectra of $Gd_4O_3F_6$:Tb^{3+}(7%) are shown in Fig. 1, which shows that the broad band at 200-240 nm is attributed to Tb^{3+} 4f-5d absorption when monitored at 541 nm.

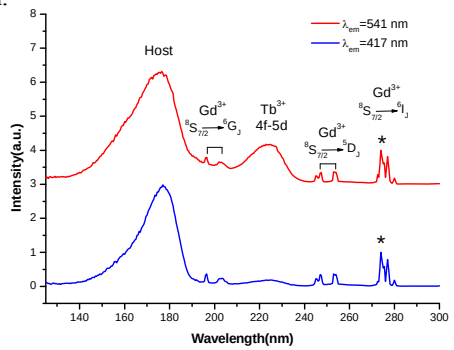

Figure 1. PLexcitation spectra of $Gd_4O_3F_6$:Tb^{3+} (7%) monitored at λ_{em} = 541 nm (red curve, $^5D_4 \rightarrow {}^7F_5$ of Tb^{3+}) and λ_{em} = 415 nm (blue curve, $^5D_3 \rightarrow {}^7F_5$ of Tb^{3+}). Both spectra are scaled to the $^8S_{7/2} \rightarrow {}^6I_J$ excitation intensity at 274 nm (*).

Fig. 2 shows multiple emissions in 360-640 nm, which were attributed to the Tb^{3+} $^5D_4 \rightarrow {}^7F_J$ transitions. When pumped at 226 nm, Tb^{3+} becomes excited to $4f^75d$ level, and subsequently relaxes from that high-lying energy level to an intermediate state $^5D_2$; the released energy is transferred to a neighboring Tb^{3+} by cross relaxation (step ①), which then serves to excite Tb^{3+} to level $^5D_4$ resulting in the observed green luminescence, based on the proposed energy level diagram of $Gd_4O_3F_6$:Tb^{3+} in Fig. 3. In addition, in the relaxation that takes Tb^{3+} from state $4f^75d$ to levels $^5D_3$, the released energy is transferred directly to the neighboring Gd^{3+} (step②), which is responsible for the observed UV luminescence of Gd^{3+} observed at 315 nm; cf. Fig. 2(a) and 2(b). Based on the PL spectra shown in Fig. 2 and equation (1), we have calculated the theoretical quantum efficiency for of $Gd_4O_3F_6$:xTb^{3+} as a function of doped Tb^{3+} concentration x and the trend of QE variation is shown in Fig. 4.

The visible QC in $Gd_4O_3F_6$:Tb^{3+} via down-conversion mechanism has been observed and investigated. The calculated QE achieves 172% under UV excitation at 226 nm. Upon excitation of Tb^{3+} with an high energy UV photon, it could be split into two photons in the visible range via a two-step process: cross relaxation and direct energy transfer. A relevant mechanism involving CR and DT processes has been proposed based on spectral data.

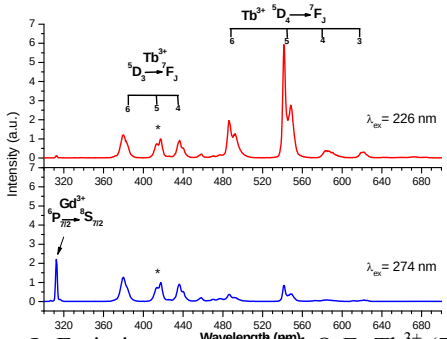

Figure 2. Emission spectra of $Gd_4O_3F_6$:Tb^{3+} (7%) excited at λ_{ex} = 274 nm (blue line) and 226 nm (red line). The spectra are scaled to the $^5D_3 \rightarrow {}^7F_5$ excitation intensity at 417 nm (*).

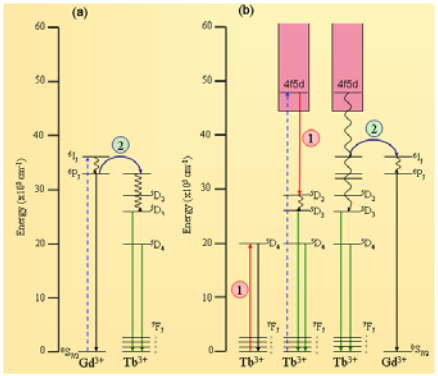

Figure 3. Energy level diagrams of $Gd_4O_3F_6$:Tb^{3+} showing possible mechanisms for visible QC under excitation of UV with λ_{ex} = (a) 274 and (b) 226 nm. ① and ② denote cross relaxation and direct energy transfer, respectively

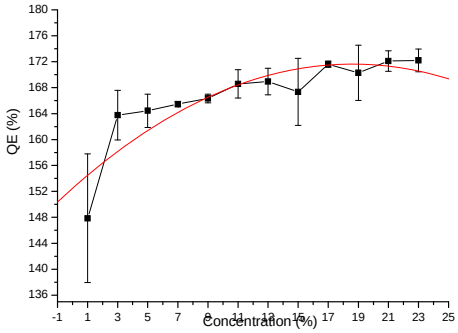

Figure 4. Calculated theoretical quantum efficiency for of $Gd_4O_3F_6$:Tb^{3+} as a function of doped Tb^{3+} concentration. The trend of QE variation is fitted with the red curve.