Visible Quantum Cutting in Tb^{3+}-doped $Ba_3Gd(PO_4)_3$ Phosphors via Downconversion

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Figure 1 presents the VUV and UV PL spectra of $Ba_3Gd(PO_4)_3$:5%Tb^{3+} upon excitation at $4f^8$-$4f^75d$ (196 and 222 nm) on Tb^{3+} and $^8S_{7/2}$-^6I_J excitation (273 nm) on Gd^{3+}, respectively. The spectra were scaled on the emission intensity of $^5D_3$-$^7F_5$ transition and we have observed that the relative intensity of the emission from $^5D_4$ levels was much stronger under the excitation to $4f^8$-$4f^75d$ levels on Tb^{3+} than that to ^6I_J (273 nm) levels on Gd^{3+}, which clearly indicates the occurrence of the QC effect in the visible spectral region. This observation shows that Tb^{3+}-pumping with high energy VUV or short-wavelength UV is equally important as Gd^{3+}-pumping in realizing visible QC of Tb^{3+}.

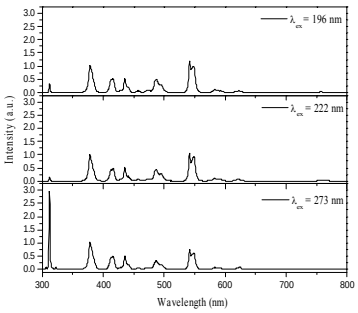

Fig. 1: Emission spectra of $Ba_3Gd(PO_4)_3$:5%Tb^{3+} upon excitation at (a) 196, (b) 222 and (c) 273 nm. The spectra are scaled on the $^5D_3$-$^7F_6$ transition of Tb^{3+}.

Figure 2 presents the VUV-UV PLE spectra of $Ba_3Gd(PO_4)_3$:5%Tb^{3+} in the range of 125 to 300 nm, monitored at $^5D_4$-$^7F_5$ emission (542 nm) and $^5D_3$ -$^7F_6$ emission (378 nm) on Tb^{3+}, respectively.

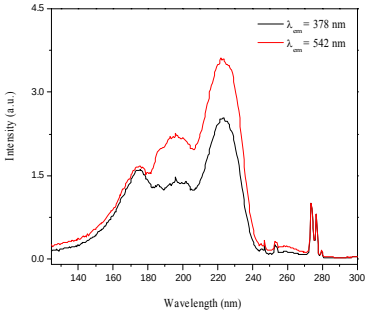

Fig. 2: Excitation spectra of $Ba_3Gd(PO_4)_3$:5%Tb^{3+} monitored at $^5D_4$-$^7F_5$ emission (542 nm) and $^5D_3$-$^7F_6$ emission (378 nm) on Tb^{3+}.

As an example, a plausible mechanism for visible quantum cutting is proposed and depicted in Fig. 3. Figure 3(a) shows that no QC occurs with λ_{ex} = 273 nm because of insufficient pumping energy. However, the observed QC process is proposed to occur in Fig. 3(b). First, cross-relaxation results from the pumping of Tb^{3+} and then the released energy from $4f^5d$ to $^5D_2$ of Tb^{3+} was used to pump a neighboring Tb^{3+}. Secondly, the direct energy transfer process is expected to occur and part of energy will then transfer between ^5D_J of Tb^{3+} and ^6I_J or ^6P_J of Gd^{3+} levels and follows the emission of $^6P_{7/2} \rightarrow {}^8S_{7/2}$.

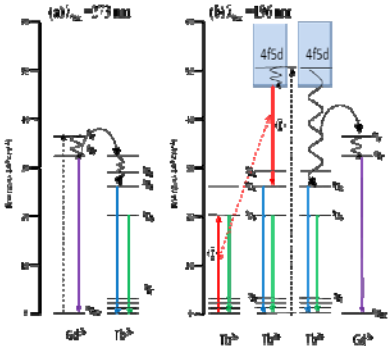

Fig. 3: Possible mechanisms for visible QC under excitation of VUV with λ_{ex} at (a) 273 and (b) 196 nm; ① and ② denote cross relaxation (CR) and direct energy transfer, respectively.

The dependence of calculated cross-relaxation efficiency on the Tb^{3+}-content of $Ba_3Gd(PO_4)_3$: x%Tb^{3+} under VUV excitation at 196 and 222 nm, respectively, are summarized in Fig. 4.

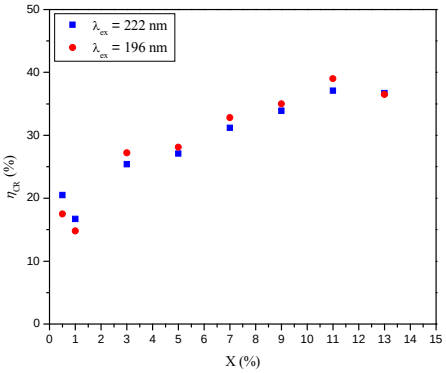

Fig. 4: Dependence of the calculated cross relaxation efficiency of Tb^{3+}-content for $Ba_3Gd(PO_4)_3$:x%Tb^{3+} under excitation of 196 and 222 nm.

In conclusion, visible QC under excitations at 222 and 196 nm through a downconversion mechanism was observed, respectively. By utilizing the Tb^{3+}-Tb^{3+} couples, QC process has been realized in $Ba_3Gd(PO_4)_3$:Tb^{3+}. The original Tb^{3+} and the neighboring Tb^{3+} and/or Gd^{3+} ions revert to their ground states by emitting two photons. Based on the PL and PLE spectra, we have calculated the theoretical quantum efficiency to be 137% and 139% under excitation at 222 and 196 nm for $Ba_3Gd(PO_4)$:5%Tb^{3+}, respectively.