

Visible quantum cutting in green-emitting BaGdF₅:Tb³⁺ phosphors via downconversion

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Abstract

The visible quantum cutting (QC) under the excitation at 215 and 187 nm in a newly discovered BaGdF₅:Tb³⁺ via downconversion mechanism has been observed and investigated. We have measured the vacuum ultraviolet (VUV) excitation and emission spectra and proposed possible mechanisms to rationalize the observed QC effect. In QC process, one short-wavelength UV or one VUV photon absorbed by Tb³⁺ was found to split into more than one visible photon emitted by Tb³⁺ through cross-relaxation and subsequent direct energy transfer between Tb³⁺ and Tb³⁺ and/or Gd³⁺ ions, depending on the excitation wavelength. On the basis of the calculations from the emission spectra in the visible region obtained, we have obtained optimal quantum efficiency as high as 168% and 180% for green-emitting BaGdF₅:Tb³⁺ under excitation at 215 and 187 nm, respectively.

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1. Introduction

Recently, considerable interest and research activities have been focused on the quantum cutting (QC) process of rare-earth-doped phosphors in the vacuum ultraviolet (VUV) region [1–10], mainly because VUV-excited phosphors are indispensable for applications of plasma display panels (PDP) and mercury-free lighting devices. However, there has been limitation in reaching high conversion efficiency from one VUV photon to one visible photon, mainly because of inherent energy loss involved in the nonradiative relaxation processes present in almost all phosphors. Regardless of the inevitable limitation, in principle, quantum efficiency (QE) as high as 200% can be achieved if phosphors can be designed so that one VUV photon can be split into two visible photons, since the energy of a VUV photon ($\lambda < 200$ nm or $E > 6.20$ eV) is more than twice the energy of a visible photon and, therefore, there is enough energy for the emission of two visible photons per each VUV photon absorbed. This

process is called quantum cutting. To fulfill the requirements of QC, the host materials must (1) possess a band gap larger than 3.0 eV and (2) the excitation energy must be higher than 6 eV ($\lambda < 200$ nm). Wide band gap fluoride materials doped with trivalent rare-earth ions can provide an excellent opportunity for developing materials suitable for applications with VUV radiation as an excitation source. In particular, the MF–GdF₃ (M = Li [3,8], Na [9], K [9,10], Cs [6]) systems have been actively investigated as successful host matrices for the design of QC phosphors, whereas AF₂–GdF₃ (A is alkaline earth metal) systems are relatively rarely investigated. Besides, the design of QC phosphors also requires appropriate combinations of R₁³⁺–R₂³⁺ or R₁³⁺–R₂³⁺–R₃³⁺ (R₁, R₂, and R₃ are rare earths) as activator ion-pairs or couples. In addition, relevant spectroscopic data are based on the energy levels for lanthanide ions in the VUV spectral range. QC via downconversion has been witnessed in many rare-earth-based phosphors [1–10]. The highest QE in the visible spectral region has been observed in LiGdF₄:Eu (190%) [3] and BaF₂:Gd,Eu (194%) [4].

Motivated by the knowledge of very limited number of QC phosphors containing Pr³⁺ [1,2] or couples of

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$\text{Gd}^{3+}\text{-Eu}^{3+}$ [3,4], $\text{Gd}^{3+}\text{-Er}^{3+}$ [5], and $\text{Gd}^{3+}\text{-Tb}^{3+}\text{-Er}^{3+}$ [6] reported previously and the search for novel phosphors showing efficient QC effect, we have investigated the $\text{MF}_2\text{-GdF}_3$ ($M = \text{Ca}, \text{Ba}$) systems doped with various rare-earth ions as activators. Regarding the crystallographic data, only the indexed XRD profile for BaGdF_5 and the phase diagram of $\text{BaF}_2\text{-GdF}_3$ have been described by Zhigarnovskii et al. [11] Our major goals are to search for new quantum cutting phosphors with improved QE for VUV phosphors up to higher than 100%. In this paper, we describe the VUV excitation and emission spectra, the results of QC through downconversion upon VUV excitation, and dependence of the efficiency of cross-relaxation between Gd^{3+} and Tb^{3+} on the Tb^{3+} -doping concentration for the recently discovered $\text{Ba}(\text{Gd}_{1-x}\text{Tb}_x)\text{F}_5$ (abbreviated as $\text{BaGdF}_5:\text{Tb}$, respectively).

2. Experimental

A series of polycrystalline samples of $\text{Ba}(\text{Gd}_{1-x}\text{Tb}_x)\text{F}_5$ ($3\% < x < 17\%$) were synthesized by sealed tube reactions from stoichiometric amount of BaF_2 , GdF_3 and TbF_3 (all 99.99% from Aldrich Chemicals, USA) at 700–900 °C for 8 h. The phase purity of $\text{Ba}(\text{Gd}_{1-x}\text{Tb}_x)\text{F}_5$ samples was then checked by using powder X-ray diffraction (XRD) analysis with a Bruker AXS D8 advanced automatic diffractometer operated at 40 kV and 30 mA with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The excitation (PLE) and photoluminescence (PL) spectra in the VUV region were measured at BL03A Station using 03A1BM-(HF-CGM) High Flux Beamline of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. For the VUV spectra measurements, CaF_2 and LiF were used as beam splitters and the spectral scan ranged from 125 to 800 nm and the spectral resolution was approximately 0.5 nm.

3. Results and discussions

The phase purity of $\text{Ba}(\text{Gd}_{1-x}\text{Tb}_x)\text{F}_5$ samples was checked by XRD and the diffraction profiles were found to be consistent with that reported by Zhigarnovskii et al. [11] Shown in Fig. 1 are the VUV and UV PL spectra of $\text{BaGdF}_5:5\%\text{Tb}^{3+}$ upon excitation at $4f^8 \rightarrow 4f^7 5d(\text{LS})$ (187 and 215 nm) on Tb^{3+} , and $^8\text{S}_{7/2} \rightarrow ^6\text{I}_J$ excitation (273 nm) on Gd^{3+} , respectively. The spectra were scaled on the emission intensity for $^5\text{D}_3 \rightarrow ^7\text{F}_6$ transition and we have observed that the relative intensity of the emission from $^5\text{D}_4$ levels was much stronger under the excitation to $4f^8 \rightarrow 4f^7 5d(\text{LS})$ levels on Tb^{3+} than that to $^6\text{I}_J$ (273 nm) levels on Gd^{3+} , which clearly indicates the occurrence of the QC effect in the visible spectral region. Furthermore, the emission centered at 310 nm can also be observed in Figs. 1a–c and attributed to the $^6\text{P}_J \rightarrow ^8\text{S}_{7/2}$ excitation transition on Gd^{3+} . This observation hints 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+} . Shown in Fig. 2 are the VUV-UV PLE spectra of

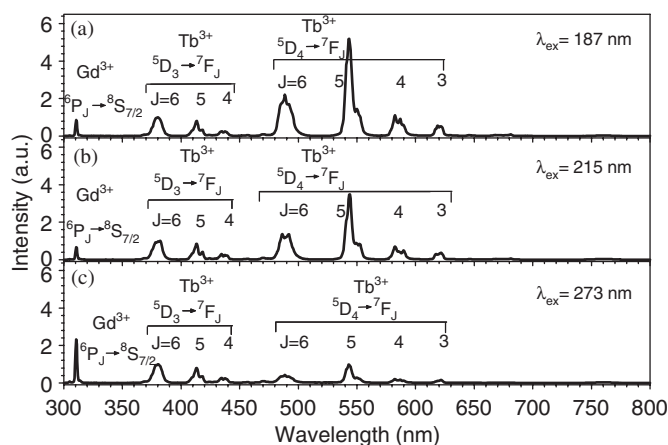


Fig. 1. VUV and UV PL spectra of $\text{BaGdF}_5:5\%\text{Tb}^{3+}$ upon excitation at $4f^8 \rightarrow 4f^7 5d(\text{LS})$ (187 and 215 nm) on Tb^{3+} (a) and (b) and $^8\text{S}_{7/2} \rightarrow ^6\text{I}_J$ excitation (273 nm) on Gd^{3+} (c).

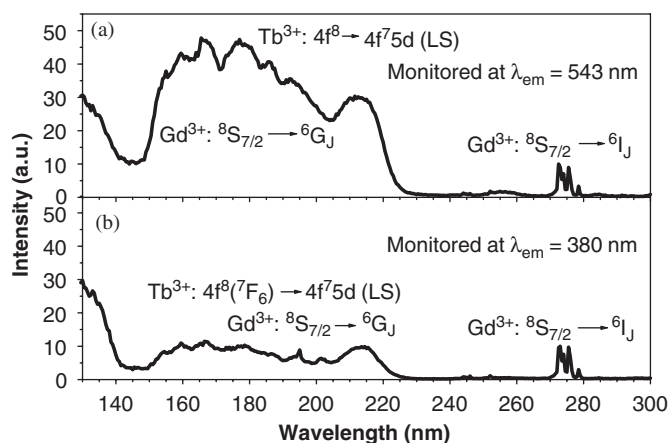


Fig. 2. VUV-UV PLE spectra of $\text{BaGdF}_5:5\%\text{Tb}^{3+}$ monitored at $^5\text{D}_4 \rightarrow ^7\text{F}_5$ emission (543 nm) and $^5\text{D}_3 \rightarrow ^7\text{F}_6$ emission (380 nm) on Tb^{3+} .

$\text{BaGdF}_5:5\%\text{Tb}^{3+}$ monitored at spin and parity-forbidden $^5\text{D}_4 \rightarrow ^7\text{F}_5$ emission (543 nm) and $^5\text{D}_3 \rightarrow ^7\text{F}_6$ emission (380 nm) on Tb^{3+} , respectively. The strong broad excitation bands spanning from 145 to 228 nm and centered at 215 and 187 nm are assigned to spin-allowed transitions from the $4f^8(^7\text{F}_6)$ to low-spin $4f^7 5d$ states of Tb^{3+} [4,13], respectively. The broadening of absorption band of Tb^{3+} at 215 nm in the excitation spectrum also supports the fact that the origin of absorption is attributed to $4f^8 \rightarrow 4f^7 5d(\text{LS})$ transitions, as described by Wegh et al. [4] and Lee et al. [12]. Furthermore, the broadening of absorption is also complicated by the overlapping of the excitation transitions attributed to $^8\text{S}_{7/2} \rightarrow ^6\text{G}_J$ of Gd^{3+} and $^7\text{F}_6 \rightarrow 4f^7 5d(\text{LS})$ of Tb^{3+} . The much weaker absorptions appearing at 256, 273, and 276 nm are assigned to the intraconfigurational excitation from the $^8\text{S}_{7/2}$ ground state to the $^6\text{D}_J$ and $^6\text{I}_J$ states of Gd^{3+} , respectively.

For the rationalization of observed QC process involved in the Tb^{3+} -pumping and/or $\text{Gd}^{3+}\text{-Tb}^{3+}$ couple of the $\text{BaGdF}_5:5\%\text{Tb}^{3+}$ phosphor, we have depicted in Fig. 3

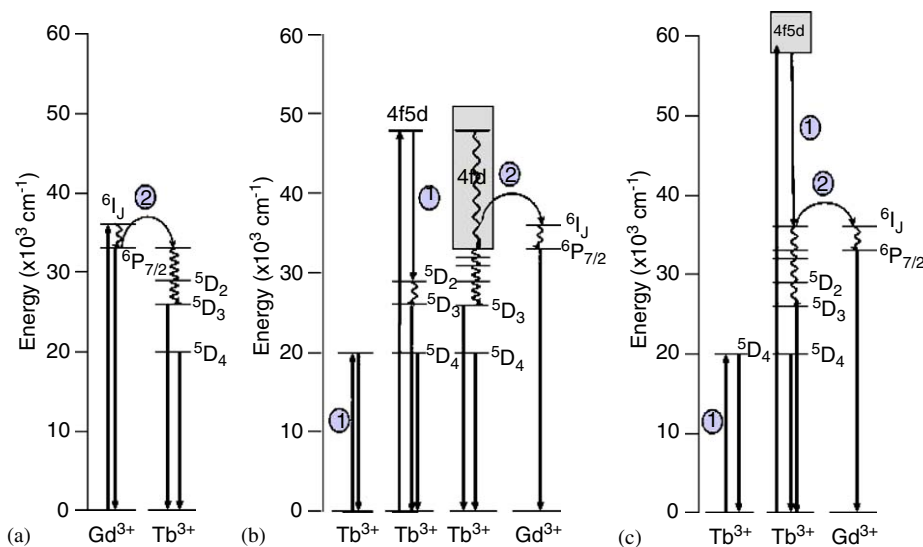


Fig. 3. Energy level diagrams for BaGdF₅:5%Tb³⁺ showing (a) no QC when λ_{ex} = 273 nm and the possible visible QC by a two-step energy transfer process when λ_{ex} = (b) 215 nm and (c) 187 nm.

three simplified energy level diagrams for BaGdF₅:5%Tb³⁺, which indicate no QC occurrence with λ_{ex} = 273 nm (Fig. 3a) and the possible visible QC by a two-step energy transfer process with λ_{ex} = 215 nm (Fig. 3b) and 187 nm (Fig. 3c), respectively, as proposed by Lee et al. [12] As revealed by the PL spectra shown in Figs. 1(a) and (b), the observed QC process is proposed to occur first through the pumping of Tb³⁺ and, subsequently, the released energy (4f5d → ⁵D₂) was used to pump a neighboring Tb³⁺ by cross-relaxation that resulted in green emission at 543 nm. Secondly, in the process of relaxation of Tb³⁺ from 4f5d to higher ⁵D_J levels, the released energy could be directly transferred from Tb³⁺ to a neighboring Gd³⁺ to generate the UV emission at 311 nm or the excited Tb³⁺ ion could further relax to the ⁵D_{3,4} levels to generate the second green-emitting photon, in which Tb³⁺ plays the role of quantum cutter by converting a VUV or UV photon into two green-emitting photons.

For the practical calculation of extra QE, some essential premises will have to be proposed. For instance, the VUV-UV absorption by phosphors cannot be taken into account. Possible nonradiative losses due to energy migration at the defects and impurities in the samples must be ignored. For overall QE calculations involved in the QC processes, in addition to the QE for direct energy transfer from (i.e., 100%), we have also calculated the extra QE corresponding to cross-relaxation from Tb³⁺ to neighboring Tb³⁺ or from Gd³⁺ to neighboring Tb³⁺ through QC by using the following equation proposed by Wegh et al. [3,4] and modified by Lee et al. [12]

$$\frac{P_{CR}}{P_{CR} + P_{DT}} = \frac{R(^5D_4/rest)_{Tb^{3+}} - R(^5D_4/rest)_{Gd^{3+}}}{R(^5D_4/rest)_{Tb^{3+}} + 1}$$

In the above equation used for QE calculation, P_{CR} represents the probability for cross-relaxation and P_{DT} is the probability for the direct energy transfer. R(⁵D₄/rest) is

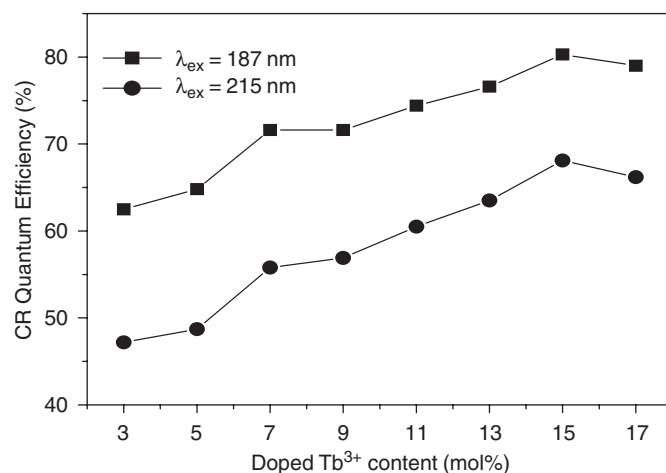


Fig. 4. The calculated cross-relaxation quantum efficiency as a function of Tb³⁺-content for BaGdF₅:xTb³⁺ under excitation of 187 and 215 nm.

the emission intensity ratio of the ⁵D₄ to those attributed to ⁵D₃ of Tb³⁺ and ⁶P_{7/2} of Gd³⁺ where the subscript indicates the excitation is from Tb³⁺ or Gd³⁺. If the QE of a phosphor via direct energy transfer is 100%, the extra QE for energy transfer via cross-relaxation is 65% and 48% for BaGdF₅:5%Tb³⁺ under the excitation of 187 and 215 nm, respectively.

We have also measured the dependence of the calculated efficiency of the cross-relaxation step on the Tb³⁺-content dependence of VUV-UV PL spectra in BaGdF₅:xTb³⁺ under VUV excitation at 187 and 215 nm, respectively, and the results are summarized in Fig. 4. The general trend indicates that the calculated cross-relaxation efficiency for BaGdF₅:xTb³⁺ phosphors was found to increase monotonically from 67% (x = 3%) to 80% (x = 15%) under the excitation at 187 nm, whereas under the excitation at 215 nm, the calculated cross-relaxation efficiency for

BaGdF₅:xTb³⁺ phosphors was observed to increase from 47% ($x = 3\%$) to 68% ($x = 15\%$).

4. Conclusion

We have synthesized and discovered a series of unprecedented quantum cutting phosphors BaGdF₅:xTb³⁺ whose visible QE has achieved 168% and 180% under excitation with UV of 215 nm and VUV of 187 nm, respectively. Upon excitation of quantum cutter Tb³⁺ with a high-energy photon, two photons in the visible range can be emitted through a two-step energy transfer (cross-relaxation and direct energy transfer) process from one Tb³⁺ to another neighboring Tb³⁺ and/or to the neighboring Gd³⁺ with a QE that exceeds 100%. However, under UV excitation of 273 nm, BaGdF₅:xTb³⁺ did not show any observable QC effect.

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