# ФИЗИЧЕСКОЕ МАТЕРИАЛОВЕДЕНИЕ

DOI: 10.18721 /JPM.10306 УДК 537.226.33

# VISIBLE QUANTUM CUTTING IN GREEN EMITTING BaF<sub>2</sub>: Gd<sup>3+</sup>, Tb<sup>3+</sup> PHOSPHORS: AN APPROACH TOWARDS MERCURY-FREE LAMPS

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Visible quantum cutting (QC) via down-conversion (DC) has been observed in the green emitting BaF<sub>2</sub> co-doped with Gd<sup>3+</sup>, Tb<sup>3+</sup> phosphors synthesized by wet chemical method. Powder X-ray diffraction (XRD) analysis showed structural purity of the synthesized phosphors. The excitation (PLE) and PL spectra in the vacuum ultraviolet (VUV) or UV region were measured with the help of 4B8-VUV spectroscopy experimental station of the Beijing Synchrotron Radiation Facility (BSRF). In the QC process, one VUV-UV photon absorbed cuts into more than one visible photons emitted by Tb<sup>3+</sup> through cross relaxation (CR) and direct energy transfer (DET) between Tb<sup>3+</sup> and Tb<sup>3+</sup> or Tb<sup>3+</sup> and Gd<sup>3+</sup>, depending on the excitation wavelength. From the emission spectra monitored at different wavelength excitation, the twostep energy transfer process was investigated, and theoretically calculated quantum efficiency observed was found to be 148 % and 177 % at the excitation wavelength of 174 nm and 219 nm respectively.

Key words: quantum cutting; inorganic phosphor; cross relaxation; energy transfer; quantum efficiency

**Citation:** S.R. Jaiswal, N.S. Sawala, K.A. Koparkar, P.A. Nagpure, V.B. Bhatkar, S.K. Omanwar, Visible quantum cutting in green emitting  $BaF_2: Gd^{3+}$ ,  $Tb^{3+}$  phosphors: an approach towards mercury-free lamps, St. Petersburg Polytechnical State University Journal. Physics and Mathematics. 10 (3) (2017) 64–74. DOI: 10.18721/JPM.10306

# ЭФФЕКТ ДАУН-КОНВЕРСИИ В ЛЮМИНОФОРАХ ЗЕЛЕНОГО СВЕЧЕНИЯ BaF<sub>2</sub>: Gd<sup>3+</sup>, Tb<sup>3+</sup> – ПЕРСПЕКТИВА ИСПОЛЬЗОВАНИЯ В БЕЗРТУТНЫХ ФЛУОРЕСЦЕНТНЫХ ЛАМПАХ

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В люминофорах  $BaF_2: Gd^{3+}$ ,  $Tb^{3+}$  с зеленым свечением, синтезированных мокрым химическим методом, наблюдалось понижение частоты кванта излучения в видимую область через процесс даун-конверсии. Анализ методом порошковой рентгеновской дифракции показал структурную чистоту синтезированных люминофоров. Спектры возбуждения и фотолюминесценции в ультрафиолетовой (УФ) и вакуумной ультрафиолетовой (ВУФ) областях измеряли на экспериментальной спектроскопической установке синхротронного излучения 4B8-VUV (г. Пекин, КНР). В процессе понижения частоты кванта один фотон из ВУФ или УФ области излучения претерпевает конверсию в более, чем один фотон люминесценции в видимой области, и эти фотоны испускаются ионами  $Tb^{3+}$  по механизмам кросс-релаксации и прямого энергопереноса между двумя ионами  $Tb^{3+}$  либо между ионами  $Tb^{3+}$  и  $Gd^{3+}$ , что зависит от длины волны возбуждающего излучения. Путем отслеживания спектров испускания при различных длинах волн возбуждающего излучения исследован двухступенчатый процесс переноса энергии. Теоретически рассчитанные максимальные значения наблюдаемого квантового выхода составили 148 и 177 % для длин волн возбуждающего излучения 174 и 219 нм соответственно.

**Ключевые слова:** понижение частоты кванта; неорганический люминофор; кросс-релаксация; энергоперенос; квантовый выход

Ссылка при цитировании: Джайсвал Ш.Р., Савала Н.С., Копаркар К.А., Нагпуре П.А., Бхаткар В.Б., Оманвар Ш.К. Эффект даун-конверсии в люминофорах зеленого свечения BaF<sub>2</sub>: Gd<sup>3+</sup>, Tb<sup>3+</sup> – перспектива использования в безртутных флуоресцентных лампах // Научно-технические ведомости СПБГПУ. Физико-математические науки. 2017. Т. 10. № 3. С. 64–74. DOI: 10.18721/JPM.10306

#### 1. Introduction

Luminescent tubes based on phosphors doped with lanthanide ions are presently useful rely on the ultraviolet (UV) excitation originating from a mercury discharge. These luminescent tubes are very popular for domestic and other purpose lighting applications. The main emission line of mercury is positioned at 254 nm. The major drawback of mercury-based fluorescent lamps is toxicity due to mercury and causes serious environmental concerns. In order to overcome these drawbacks the mercury-based discharge lamps are replaced by a xenon-based fluorescent tube. The xenon discharge has emissions in the vacuum ultraviolet (VUV), particularly the Xe resonance emission line (147 nm) and/or the Xe<sub>2</sub> molecular emission band (172 nm). The advantage of this xenon discharge is that it requires no start-up time. The phosphors presently worn in luminescent tubes do not absorb the 147 and 172 nm radiation efficiently and also undergo as of degradation upon VUV excitation. Moreover, in the conversion of one VUV photon of the xenon discharge into a visible photon more energy is lost [1].

In order to overcome these difficulties, it is necessary to develop the phosphors which absorb one high-energy VUV photon and split into two or more low energy (visible) photons; the phenomenon is known as quantum cutting (QC). The QC provides a means to obtain two or more photons for each absorbed photon [2-5]. Therefore it serves as a DC mechanism with quantum efficiency greater than unity and it offers the prospect of providing improved energy efficiency in lighting devices [6]. In order to obtain quantum-cutting phosphors with quantum efficiencies exceeding unity, the lanthanide ions are palpable candidates for this purpose due to their energy level structures that afford metastable levels from which quantumcutting processes are promising.

Shi, et al. [7] reported that the inorganic host matrix  $BaF_2$  is a crystal having broad band about 10.9 eV. The  $BaF_2$ :  $Re^{3+}$  (Ce, Pr, Tb, Eu, Dy) were studied in earlier reports [8 – 10]. The process of energy transfer (ET) and QC in  $BaF_2$ :  $Gd^{3+}$ ,  $Eu^{3+}$  can occur by the dopants combination of  $Gd^{3+}$  and  $Eu^{3+}$ , in which  $Gd^{3+}$  acts as a sensitizer, and absorbed high energy VUV photon which cuts into two visible photons emitted by two  $Eu^{3+}$  ions which act as activators. Palan, et al. [11, 12] reported terbium doped various phosphor materials.

Motivated from the above survey, here we intended to study the visible QC process under the excitation of VUV or UV radiation in BaF<sub>2</sub>:Gd<sup>3+</sup>, Tb<sup>3+</sup> phosphors synthesized via wet chemical method followed by reactive atmosphere process (RAP). Belsare, et al. [13] well discussed the RAP in their papers. Trivalent terbium ions co-doped with Gd<sup>3+</sup> ions in the BaF<sub>2</sub> host matrix are reported for the first time.

## 2. Experimental

Barium fluoride  $(BaF_2)$  co-doped with  $Gd^{3+}$ ,  $Tb^{3+}$  phosphors was prepared by

wet chemical method followed by reactive atmospheric process. In this method we used metal carbonate like  $BaCO_3$  (99.99 % AR) as a precursor. Barium carbonate was taken in the teflon beaker. A small amount of doubledistilled water was added into the beaker and stirred it, then hydrofluoric acid (HF) was added in it to get slurry. The slurry was dried by blowing air or heating on a hot plate (80°C). A freshly prepared  $BaF_2$  host was obtained.  $Gd_2O_3$ (99.9% AR) and  $Tb_2(SO_4)_3 \cdot 8H_2O$  (99.90 %, AR) were boiled in HNO<sub>3</sub> and evaporated to dryness, so as to convert them into respective nitrates. The aqueous solution of these nitrates was used as a dopant. The 1 mol % of gadolinium nitrate and 1mol % of terbium nitrate were mixed in the host material and dried completely by blowing hot air to obtain dried powder. The dried powder was transferred to a glass tube and about 2.5 wt. % RAP agent was added. In this process, we used ammonium fluoride as a RAP agent. The tube was closed with a tight stopper and slowly heated to 500°C for 2 h. The stopper was removed and the powders were transferred



Fig. 1. Flow chart of BaF<sub>2</sub>: 1% Gd<sup>3+</sup>, xTb<sup>3+</sup> (0.5%  $\leq x \leq$  7.0%) synthesized by wet chemical method



Fig. 2. XRD pattern of BaF<sub>2</sub>: 1% Gd<sup>3+</sup>, xTb<sup>3+</sup> (0.5%  $\leq x \leq$  7.0 %) synthesized by wet chemical method

to a graphite crucible pre-heated to a suitable temperature. After heating in the graphite crucible for 1 h the resulting phosphor was rapidly quenched down to room temperature [13]. The complete process involved in the reaction is presented as a flow chart in Fig. 1. The crystal structure of the phosphor powders were characterized by powder X-ray diffraction (XRD) analysis by using Rigaku miniflex II X-ray diffractometer with a scan speed of 2.000°/min and CuK ( $\lambda = 0.15406$  nm) radiation in the range from 10° to 80°. The PLE and PL spectra in the VUV region were measured at 4B8-VUV spectroscopy experimental station on beam line of the Beijing Synchrotron Radiation Facility (BSRF), P.R. China. All the measurements were performed at room temperature.

#### 3. Results and discussion

**XRD of BaF**<sub>2</sub>: 1% Gd<sup>3+</sup>, *x*Tb<sup>3+</sup>. The phase purity of BaF<sub>2</sub>: 1% Gd<sup>3+</sup>, *x*Tb<sup>3+</sup> (0.5%  $\leq x \leq$ 7.0%) samples were confirmed by XRD pattern as shown in Fig. 2. The XRD pattern of prepared phosphors matched well with ICDD file card No. 01-085-1341. From the XRD pattern, the high intensity peaks were observed at 20 = 24.87, 28.79, 41.17, 48.70, 51.02, 59.6, 65.62 and 67.55 degrees which correspond to (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1) and (4 2 0) diffraction planes respectively.

Photoluminescence properties of BaF<sub>2</sub>:

1% Gd <sup>3+</sup>, *x*Tb<sup>3+</sup>. The concentration quenching of Gd<sup>3+</sup> as a sensitizer in the BaF<sub>2</sub> host matrix was first determined. From Fig. 3 it can be advocated that at 1 mol % of Gd<sup>3+</sup> ions in BaF<sub>2</sub> the host shows optimum intensity peak at 310 nm under an excitation wavelength of 274 nm [14].

Fig. 4, a shows VUV-UV excitation spectra of photoluminescence (PLE spectra) of BaF<sub>2</sub>: 1% Gd <sup>3+</sup>, xTb<sup>3+</sup> (0.5 %  $\leq x \leq$  7.0 %) in the range from 125 to 300 nm. All the excitation spectra are the same except for their intensities. The spectra were obtained by monitoring at the transition of  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  of  $Tb^{3+}$ , with an emission wavelength of 543 nm. The spectra consist of two bands and one small intensity peak. The first broad excitation band ranging from 150 to 190 nm and second excitation band ranging from 200 to 240 nm are centered at 174 and 219 nm, respectively. They are assigned to spin-allowed transitions from the 4f  ${}^{8}({}^{7}F_{6})$  to low-spin 4f  ${}^{7}5d$  states of Tb<sup>3+</sup> [15, 16]. The broadening of the absorption band of Tb<sup>3+</sup> at 219 nm in the excitation spectrum also supports the fact that the origin of absorption is attributed to  $4f^8 \rightarrow 4f^7 5d$  (LS) transition, as described by Wegh, et al. [15] and Lee, et al. [17]. Besides, the broadening of the absorption band is also complicated by the overlapping of the excitation transitions accredited to  ${}^{8}S_{7/2} \rightarrow {}^{6}G_{J}$  of Gd<sup>3+</sup> and  ${}^{7}F_{6} \rightarrow 4f$   ${}^{7}5d$  (LS) of Tb<sup>3+</sup>. The one small intensity peak at 274 and



Fig. 3. Photoluminescence emission spectra of BaF<sub>2</sub>: x Gd<sup>3+</sup> under an excitation wavelength of 274 nm; x = 0.5 % (1), 1.0 % (2), 1.5 % (3), 2.0 % (4), 3.0 % (5)



Fig. 4. VUV-UV PLE spectra monitored by the emission line of Tb<sup>3+</sup> at 543 nm (*a*); PL spectra of the BaF<sub>2</sub>: 1% Gd<sup>3+</sup>, xTb<sup>3+</sup> (0.5%  $\leq x \leq$  7.0%) phosphor excited at 274 nm (*b*), 219 nm (*c*) and 174 nm (*d*), respectively. x = 0.5% (*I*), 1.0% (*2*), 3.0% (*3*), 7.0% (*4*)

278 nm are accredited to the  ${}^{8}S_{7/2}$  ground state to the  ${}^{6}D_{J}$  and  ${}^{6}I_{J}$  states of Gd<sup>3+</sup>, respectively.

The measured emission spectra of BaF<sub>2</sub>: 1% Gd<sup>3+</sup>, *x*Tb<sup>3+</sup> (0.5%  $\leq x \leq$  7.0%) monitored at 274, 219 and 174 nm are shown in Fig. 4, *b*, *c* and *d*. The emissions could be accredited to  ${}^{5}D_{3} \rightarrow {}^{7}F_{J}$  (J = 2, 3, 4, 5 and 6) and  ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$  (J = 3, 4, 5 and 6) transitions of Tb<sup>3+</sup> ions among which the transition  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ leads to the green emission at a wavelength of 543 nm. The  ${}^{5}D_{4}$  emission of Tb<sup>3+</sup> increased while the  ${}^{5}D_{3}$  emission decreased with an increase in the Tb<sup>3+</sup> content, which is due to the cross relaxation between the  ${}^{5}D_{3} \rightarrow {}^{5}D_{4}$ transition and  ${}^{7}F_{6} \rightarrow {}^{7}F_{0}$  transition of Tb<sup>3+</sup> [18, 19]. The  ${}^{5}D_{4}$  emission of Tb<sup>3+</sup> increased rapidly with an increase in the concentration of Tb<sup>3+</sup>. This is due to numerous factors along with the cross relaxation between the  ${}^{5}D_{3}$  and  ${}^{5}D_{4}$  levels since luminescence centers increase



Fig. 5. Energy level diagrams for BaF<sub>2</sub>: 1% Gd <sup>3+</sup>, xTb<sup>3+</sup> showing the mechanism for visible quantum cutting and the energy transfer process excited at 274(*a*), 219(*b*) and 174 nm(*c*)
(1), (2) represent cross relaxation and direct energy transfer mechanisms, respectively; 3,4 correspond to green and UV emission lines, respectively

with concentration of  $Tb^{3+}$  ions in the host matrix.

Quantum cutting in BaF<sub>2</sub>: 1% Gd <sup>3+</sup>, *x*Tb<sup>3+</sup>. In the QC process, one VUV-UV photon absorbed by  $Tb^{3+}$  ion "splits" into more than one visible photons emitted by Tb<sup>3+</sup> through a cross-relaxation energy transfer (CRET) and a direct energy transfer (DET) between two Tb<sup>3+</sup> ions or Tb<sup>3+</sup> and Gd<sup>3+</sup> ions, depending on the excitation wavelength, was observed in BaF<sub>2</sub>: 1% Gd<sup>3+</sup>, Tb<sup>3+</sup> samples. Fig. 5 shows three simplified energy level diagrams for  $Ba_{(0.99-x)}F_2$ : 1% Gd<sup>3+</sup>, xTb<sup>3+</sup>. No quantum cutting occurs in BaF<sub>2</sub>: 1% Gd <sup>3+</sup>, xTb<sup>3+</sup> with excitation of the  ${}^{8}S_{7/2} \rightarrow {}^{6}I_{J}$  level of Gd<sup>3+</sup> (274 nm) as shown in Fig. 5, *a*. When  $Tb^{3+}$  ions in the host matrix are excited to their  $4f^{7}5d^{1}$  states, the QC process can be realized by two steps: cross relaxation mechanism (step 1 is indicated by number 1 in the circle) and DET (step 2 is indicated by number 2 in the circle) as shown in Fig. 5, band c. As revealed by the PL spectra shown in Figs. 6, *a*, *b* and *c*, the QC process is proposed to occur firstly through the pumping of  $Tb^{3+}$ and, afterwards, the released energy owing to  $4f5d \rightarrow {}^{5}D_{3}$  transition was used to pump a neighboring Tb<sup>3+</sup> by cross-relaxation (indicated by lines number 1) that resulted in green emission at 543 nm (indicated by lines 3).

Secondly, in the process of relaxation of Tb<sup>3+</sup> from 4*f*5*d* to higher <sup>5</sup>*D<sub>j</sub>* levels, the released energy could be directly transferred from Tb<sup>3+</sup> ion to a neighboring Gd<sup>3+</sup> ion to generate the UV emission at 311 nm (indicated by lines *4*) or the excited Tb<sup>3+</sup> ion could further relax to the <sup>5</sup>*D*<sub>3, 4</sub> levels to generate the second green emitting photon (indicated by line *3*), in which Tb<sup>3+</sup> plays the role of activator by converting a VUV or UV photon into two green-emitting photons [20].

In the second step, i.e. the process of relaxation of  $Tb^{3+}$  from 4f5d to higher  ${}^5D_J$  levels, the released energy utilized to excite  $Tb^{3+}$ ion could further relax to the  ${}^5D_{3, 4}$  levels with increasing the  $Tb^{3+}$  ions concentration in the host matrix.

The extra quantum efficiency  $\eta$  corresponding to cross relaxation can be theoretically calculated by the emission spectra, and some essential premises are proposed that,



Fig. 6. VUV and UV PL spectra of BaF<sub>2</sub>: 1% Gd<sup>3+</sup>, 3% Tb<sup>3+</sup> upon excitation at  $4f^8 \rightarrow 4f^75d(\text{LS})$  (*a*) and  $f \rightarrow d$  (LSA) (*b*) transitions (174 nm (*a*) and 219 (*b*) nm) on Tb<sup>3+</sup>, and at  ${}^8S_{7/2} \rightarrow {}^6I_J$  excitation (274 nm) on Gd<sup>3+</sup>(*c*)

the VUV absorption of phosphors should not be taken into account and possible nonradiative losses due to energy migration over defects and impurities in samples must be ignored [20]. For calculations of theoretical value of QE involved in the QC processes, in addition to  $\eta_{DT}$  (i.e., 100 %), we have calculated the extra QE equivalent to cross relaxation ( $\eta_{QC}$ ) from Tb<sup>3+</sup> ion to a neighboring Tb<sup>3+</sup> ion through QC with the following equation proposed by Wegh, et al. [15, 21 – 24] and modified by Lee, et al. [17]:

$$\eta_{\rm QC} = \eta + \eta_{\rm DT},$$
$$\eta = \frac{P_{\rm CR}}{P_{\rm CR} + P_{\rm DT}} =$$

$$=\frac{R({}^{5}D_{4} / \text{rest})_{\text{Tb}^{3+}} - R({}^{5}D_{4} / \text{rest})_{\text{Gd}^{3+}}}{R({}^{5}D_{4} / \text{rest})_{\text{Tb}^{3+}} + 1}$$

Here  $P_{CR}$ ,  $P_{DT}$  represent the probabilities for cross relaxation (CR) and direct energy (DE) transfer mechanisms, respectively;  $R({}^{5}D_{4}/\text{rest})$  is the ratio of PL intensity of  ${}^{5}D_{4}$  to that accredited to  ${}^{5}D_{3}$  of Tb<sup>3+</sup> and  ${}^{6}P_{7/2}$  of Gd<sup>3+</sup> where the subscripts indicate the excitation from Tb<sup>3+</sup> or Gd<sup>3+</sup>. If the QE of a phosphor via DET is 100%, from the integrated peak intensity then the cross relaxation efficiency of the phosphor was calculated theoretically.

The CRET efficiency increases with an increase in  $Tb^{3+}$  content in the host matrix and, according to calculations, maximum quantum

efficiency (QE) was calculated to be 148 % and 177% under the excitation wavelength of 174 and 219 nm, respectively, at 3% of Tb<sup>3+</sup> ions concentration. The cross-relaxation efficiency decrease at x = 7 % concentration of Tb<sup>3+</sup> may be due to a high concentration of defects or impurities in the host matrix [25].

### 4. Conclusions

The Ba<sub>(0.99-x)</sub>F<sub>2</sub>: 1% Gd <sup>3+</sup>, *x*Tb<sup>3+</sup> (0.5 %  $\leq x \leq \leq$  7.0 %) phosphors were successfully prepared by the wet chemical method under RAP. Visible quantum cutting through down conversion has been observed in BaF<sub>2</sub>: 1% Gd <sup>3+</sup>, *x*Tb<sup>3+</sup> phosphor. The quantum efficiency of BaF<sub>2</sub>: 1% Gd<sup>3+</sup>, *x*Tb<sup>3+</sup> phosphor was calculated and the optimal theoretical quantum efficiency was found to be 148 and 177 % under the excitation of 174 and 219 nm, respectively, for 3 % of Tb<sup>3+</sup> ions. From the above investigational

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report we conclude that the phosphors  $BaF_2$ :  $Gd^{3+}$ ,  $Tb^{3+}$  can be an excellent potential candidate for the applications in Hg-free fluorescent lamps, plasma display panels and 3D PDPs technology.

## Acknowledgements

We appreciative to 4B8 VUV spectroscopy beam line scientists of Beijing Synchrotron Radiation Facility (BSRF), P.R. China, for providing that access for recording VUV on beamline 4B8 under dedicated synchrotron mode using remote access mode. One of the authors, S.R. Jaiswal, is thankful to the chairman of FIST-DST project, Department of Physics, Sant Gadge Baba Amravati University, Amravati, for providing necessary facilities, and the authors are also thankful to Dr. G.V. Korpe, Department of Chemistry, Shri Shivaji Science College, Akola, for moral and official supports.

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Received 27.04.2017, accepted 26.06.2017.

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Статья поступила в редакцию 27.04.2017, принята к публикации 26.06.2017.

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Научно-технические ведомости СПбГПУ. Физико-математические науки 10(3) 2017

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