



## Energy Transfer and Visible Quantum Cutting in BaF<sub>2</sub> co-doped with Gd<sup>3+</sup>, Eu<sup>3+</sup> Phosphor synthesis via wet chemical method followed by Reactive Atmosphere Process

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### Abstract

BaF<sub>2</sub> co-doped with Gd<sup>3+</sup>, Eu<sup>3+</sup> was prepared via wet chemical method. Powder X-ray diffraction analysis showed structural purity of the as-synthesized phosphor. The emission and excitation spectra of BaF<sub>2</sub>:Gd<sup>3+</sup>, Eu<sup>3+</sup> were investigated using the VUV beam line of the Beijing Synchrotron Radiation Facility (BSRF), China. The energy transfer in barium fluoride from Gd<sup>3+</sup> ions to Eu<sup>3+</sup> occurs through cross relaxation. According to calculations from the emission spectra under different wavelength excitations, the two-step energy transfer process with visible quantum efficiency was found to be 130% under excitation at 161 nm in reactive atmosphere process.

**Keywords:** wet chemical method, Reactive Atmosphere Process (RAP), Energy transfer, VUV spectroscopy.

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### 1. INTRODUCTION

In order to acquire higher energy efficiency than a mercury-based discharge lamp, a xenon-based fluorescent tube needs phosphors with visible quantum efficiency higher than 100%. This is possible due to quantum cutting (QC) phosphor, which upon VUV excitation emits two (visible) photons, for each VUV photon absorbed. Quantum cutting provides a means to obtain two or more photons for each photon absorbed. Therefore it serves as a down converting (DC) mechanism with quantum efficiency greater than unity and it offers the prospect of providing improved energy efficiency in lighting devices [1]. For obtaining quantum-cutting phosphors with quantum efficiencies exceeding unity, the lanthanide ions are probable candidates due to their energy level structures that afford metastable levels, from which quantum-cutting processes are promising. The VUV levels of many of the lanthanides have been recently measured, providing the starting point from which new phosphors may be designed [2]. In our experiments, we used gadolinium and europium as dopants in BaF<sub>2</sub>. Shi. *et al.* reported that the inorganic host matrix BaF<sub>2</sub> is a broad band gap crystal having band gap about 10.9 eV [3]. BaF<sub>2</sub>:RE<sup>3+</sup> (Ce, Pr, Tb, Eu, Dy) was studied earlier reports [4-6]. The process of energy transfer and

quantum cutting in BaF<sub>2</sub>: Gd<sup>3+</sup>, Eu<sup>3+</sup> can occur by the dopant combination of Gd<sup>3+</sup> and Eu<sup>3+</sup>, in which Gd<sup>3+</sup> acts as a sensitizer and absorbs high energy VUV photon, which is cut into two visible photons emitted by two Eu<sup>3+</sup> ions (activator).

### 2. EXPERIMENTAL

Barium fluoride co-doped with Gd<sup>3+</sup>, Eu<sup>3+</sup> phosphor was prepared by wet chemical method followed by reactive atmospheric process. In this method, we used metal carbonate like BaCO<sub>3</sub> (99.99% A.R.) as a precursor. Barium carbonate was taken in Teflon beaker. A small amount of double distilled water was added in beaker and stirred; then hydrofluoric acid (HF) was added in it to get slurry. The slurry was dried by blowing air or heating on hot plate (80°C). A freshly prepared BaF<sub>2</sub> host was obtained. Gd<sub>2</sub>O<sub>3</sub> (Loba 99.9%) and Eu<sub>2</sub>O<sub>3</sub> (Loba 99.9%) 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 were used for doping. The 1 mol% of gadolinium nitrate and 1mol% of europium nitrate were mixed in the host material and the slurry was dried completely.

The dried powder was transferred to a glass tube and about 1.0 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 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 to room temperature. Belsareet *al.* have discussed about RAP in their literature [7]. The complete process involved in the reaction was represented as a flow chart in Fig. 1.

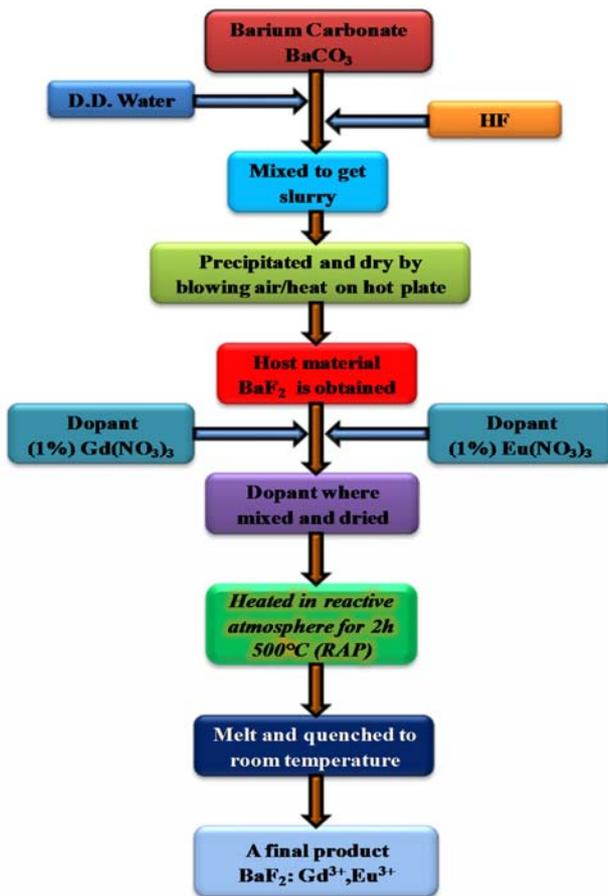


Fig.1. Flow chart of BaF<sub>2</sub>: Gd<sup>3+</sup>, Eu<sup>3+</sup> synthesized by RAP.

### 3. RESULTS AND DISCUSSION

#### 3.1 XRD Analysis

The formation of the BaF<sub>2</sub>:Gd<sup>3+</sup>, Eu<sup>3+</sup> sample in the crystalline phase synthesized by wet chemical method was confirmed by XRD pattern as shown in Fig.2. The XRD pattern for BaF<sub>2</sub>:Gd<sup>3+</sup>, Eu<sup>3+</sup> agreed well with the standard data from ICDD file (01-085-1341). The XRD pattern shows that BaF<sub>2</sub> lattice possesses cubic structure with a space group *Fm-3m* (225) with lattice parameters  $a = b = c = 6.1964 \text{ \AA}$  and interfacial angles  $\alpha = \beta = \gamma = 90^\circ$ .

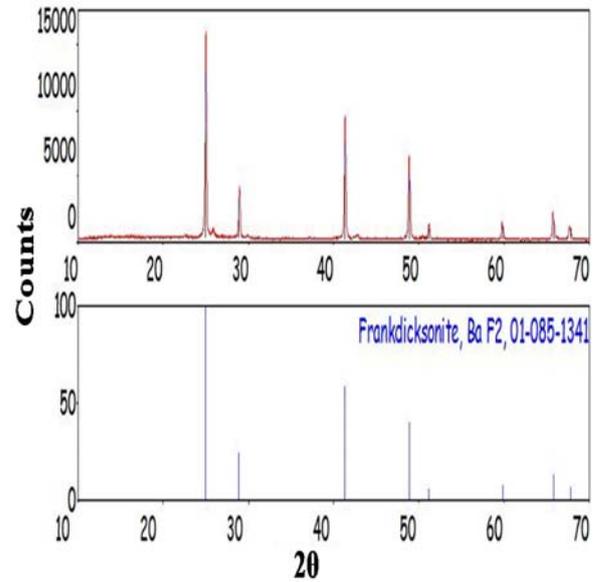


Fig.2.XRD patterns of BaF<sub>2</sub>: Gd<sup>3+</sup>, Eu<sup>3+</sup> synthesized by RAP.

#### 3.2 VUV-UV PL Analysis

The concentration quenching of Gd<sup>3+</sup> as a sensitizer in BaF<sub>2</sub> host matrix was determined. From Fig.3, it can be advocated that at 1 mol% of Gd<sup>3+</sup> ions in BaF<sub>2</sub> host show optimum intensity peak at 311 nm under the excitation of 273 nm. There are excitation lines peaking at about 161, 196, 202, 251 and 274 nm responsible for <sup>8</sup>S<sub>7/2</sub>→<sup>6</sup>G<sub>J</sub>, <sup>6</sup>D<sub>J</sub>, <sup>6</sup>I<sub>J</sub> respectively as shown in Fig 4. [8].The emission spectra under excitation 274, 172 and 161 nm are shown in Fig 5. The emission lines of Eu<sup>3+</sup> peaked at about 593, 613, 650 and 700nm correspond to <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>J</sub> (J=1, 2, 3, 4) transitions respectively and the <sup>5</sup>D<sub>1</sub>→<sup>7</sup>F<sub>J</sub> transition peaks of Eu<sup>3+</sup> are much weaker than those of <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>J</sub> transition as shown in Fig 5.

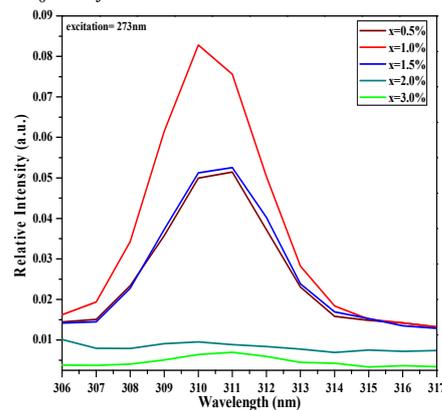


Fig.3.Emission spectra of BaF<sub>2</sub>: x% Gd<sup>3+</sup> under the excitation of 273 nm.

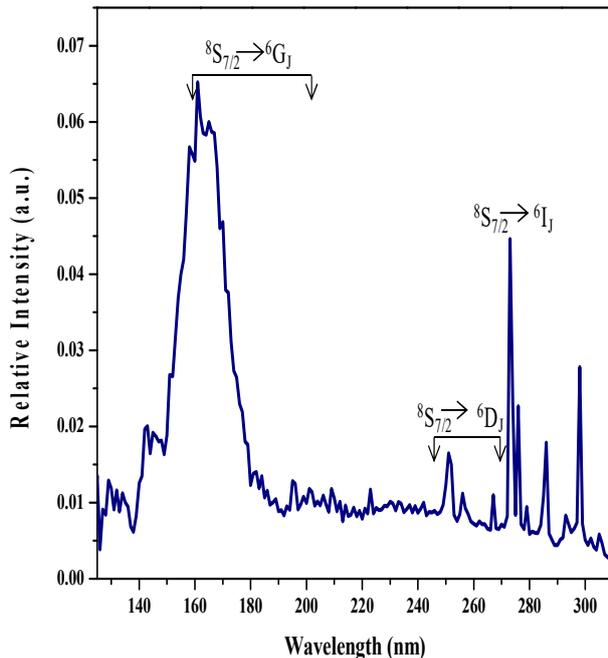


Fig.4. Excitation spectrum of BaF<sub>2</sub>: Gd<sup>3+</sup>, Eu<sup>3+</sup> monitored at 593 nm.

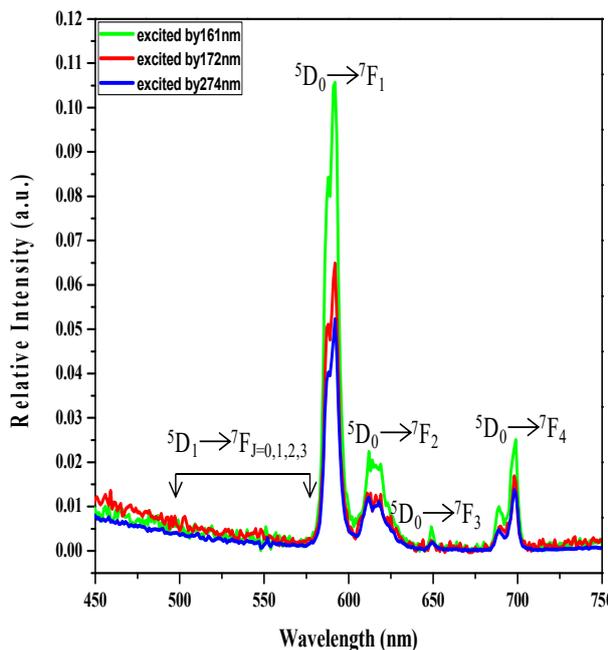


Fig.5. Emission spectra of BaF<sub>2</sub>: Gd<sup>3+</sup>, Eu<sup>3+</sup> at excitation wavelengths 161, 172 and 274 nm.

The process of energy transfer and quantum cutting can occur by the combination of Gd<sup>3+</sup> and Eu<sup>3+</sup> in which Gd<sup>3+</sup> acts as a sensitizer, absorbing a VUV photon corresponding to  $8S_{7/2} \rightarrow 6G_1$ . The absorbing high energy photon is cut into two visible photons (two red light photons) emitted by two Eu<sup>3+</sup>

ions acts as an activator. The energy of transitions  $6G_J \rightarrow 6P_J$  on Gd<sup>3+</sup> matches the  $7F_J \rightarrow 5D_0$  excitation energy on Eu<sup>3+</sup>. Upon excitation in the  $6G_J$  levels of Gd<sup>3+</sup> as the first step, energy is transferred by cross-relaxation between Gd<sup>3+</sup> and Eu<sup>3+</sup>, which causes Gd<sup>3+</sup> to fall into the  $6P_J$  state and Eu<sup>3+</sup> is excited into the  $5D_0$  state. The excited Eu<sup>3+</sup> is responsible for the first visible photon. The first step is called as resonant energy migration. In the second step, the remaining excitation energy of Gd<sup>3+</sup> in the  $6P_J$  state is transferred to another nearing Eu<sup>3+</sup> ion, i.e. Eu<sup>3+</sup> ion exciting into a high state. Then a fast relaxation from a high excited state to  $5D_J$  states will occur. After the first step, because Eu<sup>3+</sup> ion only is excited into  $5D_0$  state, only the emissions of  $5D_0 \rightarrow 7F_J$  transitions are expected. Nevertheless after the second step, all levels of  $5D_{3,2,1,0}$  of Eu<sup>3+</sup> are probably occupied, so the emission wavelength consists of all of the  $5D_J$  ( $J=0,1,2,3$ )  $\rightarrow 7F_J$  transitions [9].

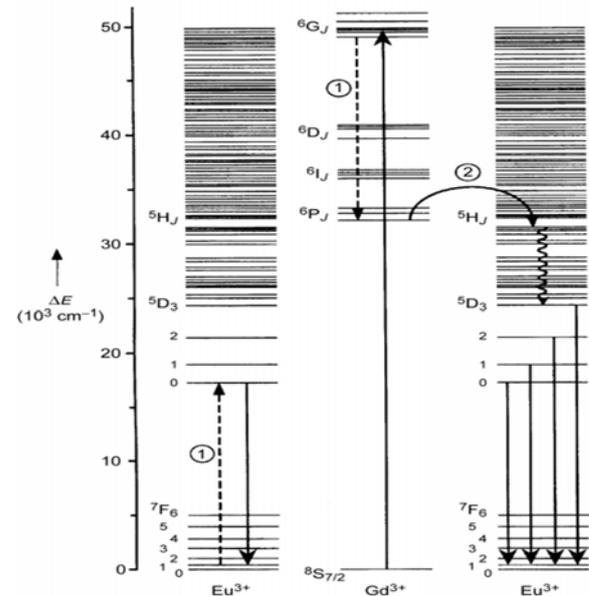


Fig.6. Energy level diagrams of Eu<sup>3+</sup> and Gd<sup>3+</sup> showing the cross-relaxation energy transfer process that leads to quantum splitting [2, 10]

In order to calculate the number of photon emitted to number of photon absorbed by the phosphor material (the term called quantum efficiency), some presumption is proposed. The VUV photon absorption efficiency cannot be taken into consideration. Some non-radiative losses at defects and impurities are ignored. In the experiment, different excitations are adopted including the excitation of Gd<sup>3+</sup>  $\rightarrow 6G_J$  with 161, 172, 202 nm and the excitation of Gd<sup>3+</sup>  $\rightarrow 6I_J$  with 273 nm. Upon



excitation in  ${}^6I_1$  level with 273 nm, the quantum cutting never occurs because no cross-relaxation exists, so the  ${}^5D_J \rightarrow {}^7F_J$  transitions emission of  $\text{Eu}^{3+}$  has a normal branching ratio between  ${}^5D_0$  and  ${}^5D_{1,2,3}$ . Upon excitation in  ${}^6G_1$  level with 161 nm, the quantum cutting can occur through a two-step energy transfer. In the second step, the emission of  $\text{Eu}^{3+}$  has a normal branching ratio. The first step will lead to the increase of  ${}^5D_0$  emission. So the ratio of  ${}^5D_0$  and  ${}^5D_{1,2,3}$  emissions is expected to increase. To determine the efficiency of the cross relaxation, the formula proposed by Wegh [11-17] was adopted as follows:

$$\frac{P_{CR}}{P_{CR} + P_{DT}} = \frac{R({}^5D_0/{}^5D_{1,2,3})_{6G_1} - R({}^5D_0/{}^5D_{1,2,3})_{6I_1}}{R({}^5D_0/{}^5D_{1,2,3})_{6I_1} + 1}$$

Where  $P_{CR}$  is the possibility for cross-relaxation,  $P_{DT}$  is the possibility for the direct transfer from  $\text{Gd}^{3+}$  to  $\text{Eu}^{3+}$ .  $R({}^5D_0/{}^5D_{1,2,3})$  is the ratio of the  ${}^5D_0$  and  ${}^5D_{1,2,3}$  emission integral intensities. The subscript ( ${}^6G_1$  or  ${}^6I_1$ ) represents the excitation level for which the ratio is observed. From the emission spectra, the value of  $R({}^5D_0/{}^5D_{1,2,3})_{6G_1}$  and  $({}^5D_0/{}^5D_{1,2,3})_{6I_1}$  can be calculated to be 33.73 and 23.30, respectively. Therefore, the value of  $P_{CR}/P_{CR} + P_{DT}$  is 0.30. It means that 30%  $\text{Gd}^{3+}$  ions in the  ${}^6G_1$  excited state settle down through a two-step energy transfer emitting two visible photons in this method. So the quantum cutting efficiency of 130% can be obtained. Quantum cutting in the Gd to Eu arrangement requires energy transfer over the Gd sublattice to Eu. Therefore if we anticipate to observe the effective quantum cutting, the concentration of Gd as an absorber or donor of energy should be more than that of Eu and make sure to migration their energy to  $\text{Eu}^{3+}$  ions competently. But in the experiment part, the concentrations of the Gd and Eu are both 1 mol %, the quantum cutting still occurs successfully, because trivalent ions tend to gather in  $\text{BaF}_2$ , which induces a local high concentration of Gd and Eu in host. For now, the distance between Eu and Gd ions will decrease due to their clustering so the energy transfer of Gd to Eu can turn into more capable process[10].

#### 4. CONCLUSIONS

The material  $\text{BaF}_2: \text{Gd}^{3+}, \text{Eu}^{3+}$  was successfully prepared through wet chemical method. The XRD pattern confirmed its cubic structure. The concentration quenching of  $\text{Gd}^{3+}$  ions in  $\text{BaF}_2$  host matrix was found to be at 1 mol%. The downconversion energy transfer was observed in  $\text{BaF}_2: 1\% \text{Gd}^{3+}, 1\% \text{Eu}^{3+}$  and the quantum efficiency was found to be around 130% under the excitation of

161 nm corresponding  ${}^8S_{7/2} \rightarrow {}^6G_1$  transition of  $\text{Gd}^{3+}$  ions.

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