



## VISIBLE QUANTUM CUTTING & DOWN-CONVERSION IN $\text{CaF}_2$ : $\text{Gd}^{3+}$ , $\text{Eu}^{3+}$ PHOSPHOR

S. R. Jaiswal<sup>1</sup>, P.A. Nagpure<sup>2</sup>, V. B. Bhatkar<sup>2</sup>, S. K. Omanwar<sup>3</sup>

<sup>1</sup>Department of Physics, Shri R. L. T. College of Science, Akola. 444606(INDIA)

<sup>2</sup>Department of Physics, Shri Shivaji Science College, Amravati. 444601 (INDIA)

<sup>3</sup>Department of Physics, SantGadge Baba Amravati University, Amravati. 444602 (INDIA)

(Corresponding author: srjaiswal07@gmail.com)

### ABSTRACT :

The conversion of vacuum ultraviolet (VUV) radiation to visible (VIS) light is described which makes it possible to obtain two VIS photons for each vacuum ultraviolet (VUV) photon absorbed. Often it is termed as Quantum Cutting (QC). The phenomenon also called as down conversion (DC), is demonstrated by  $\text{CaF}_2$ :  $\text{Gd}^{3+}$ ,  $\text{Eu}^{3+}$ . We prepared  $\text{CaF}_2$ :  $\text{Gd}^{3+}$ ,  $\text{Eu}^{3+}$  phosphor synthesis via reactive atmosphere process. Powder X-ray diffraction analysis shows structural purity of as-synthesized phosphor. The emission and excitation spectra of  $\text{CaF}_2$ : $\text{Gd}^{3+}$ ,  $\text{Eu}^{3+}$  were investigated using the VUV beam line of the Beijing Synchrotron Radiation Facility (BSRF), China. The energy transfer (ET) in calcium fluoride compound from the  $\text{Gd}^{3+}$  ions to  $\text{Eu}^{3+}$  through cross relaxation occurs. On the basis of the calculations from the emission spectra in the visible region obtained, we have obtained optimal quantum efficiency as high as 117% for red-emitting  $\text{CaF}_2$ : $\text{Gd}^{3+}$ ,  $\text{Eu}^{3+}$  phosphor under excitation of 203 nm in reactive atmosphere process (RAP).

**KEYWORDS:** Reactive Atmosphere Process (RAP), Quantum cutting, VUV spectroscopy, Energy transfer,  $\text{CaF}_2$ .

### 1. INTRODUCTION

For the development of mercury free fluorescent lamps and plasma display panels (PDPs), we require phosphor having quantum efficiency is greater than unity under VUV excitation. The phosphors having quantum efficiency is greater than unity are called quantum cutting phosphors. Quantum cutting provides a means to obtain two or more low energy photons for each high energy absorbed photon. Therefore it serves as a down converting (DC) mechanism with quantum efficiency greater than unity and it offers the prospect of providing enhanced energy effectiveness in lighting devices [1]. In order to obtain quantum-cutting phosphors with quantum efficiencies exceeding unity, the lanthanide ions are obvious candidates for this purpose due to their energy level structures that afford metastable levels from which quantum-splitting processes are capable. The inorganic calcium fluoride is one of the most important host with certain weird characteristics like wide band gap greater than 11 eV. Calcium fluoride with rare earth doped phosphor has conventional attention for numerous research works [3]. B. Herdenet *et al.* reported photon cascade emission in  $\text{Pr}^{3+}$ -doped fluorides with  $\text{CaF}_2$  structure [4]. W. Binder *et al.* reported  $\text{CaF}_2$ : $\text{Sm}^{3+}$  Phosphor was used for the application of solid state laser materials [5]. A. Lucas discussed  $\text{CaF}_2$ : Dy and  $\text{CaF}_2$ : Tm phosphors are used for the application of dosimetry [6]. In our experiments we use gadolinium and europium lanthanides as a dopant in the host of  $\text{CaF}_2$  for the application of quantum cutting. The process energy transfer and quantum cutting in  $\text{CaF}_2$ :  $\text{Gd}^{3+}$ ,  $\text{Eu}^{3+}$  can occur by the dopant combination of  $\text{Gd}^{3+}$  and  $\text{Eu}^{3+}$ , in which  $\text{Gd}^{3+}$  (acts as a sensitizer) and absorbing high energy VUV photon is cut into two visible photons emitted by two  $\text{Eu}^{3+}$  ions (acts as an activator).

## 2. EXPERIMENTAL

CaF<sub>2</sub>: Gd<sup>3+</sup>, Eu<sup>3+</sup> phosphor was synthesis via reactive atmospheric process. In this method we used metal carbonate like CaCO<sub>3</sub> (99.99% A.R.) as a precursor. The inorganic calcium carbonate was taken in Teflon beaker. A little amount of double distilled water was added in beaker and stirred it, then hydrofluoric acid (HF) added in it to get slurry. The slurry was dried by blowing air or heating on hot plate (80°C). A freshly prepared CaF<sub>2</sub> host was obtained. Gd<sub>2</sub>O<sub>3</sub> (AR 99.9%) and Eu<sub>2</sub>O<sub>3</sub> (AR 99.9%) were boiled in HNO<sub>3</sub> and evaporated to dryness, so as to convert them into relevant nitrates. The aqueous solution of these nitrates where use as a dopants. The 1 mol% of gadolinium nitrate and 1mol% of europium nitrate where assorted in the host material and dehydrated 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. Belsare *et al.* well discussed about RAP in their literature [7]. The complete process involved in the reaction was represented as a flow chart in Fig. 1.

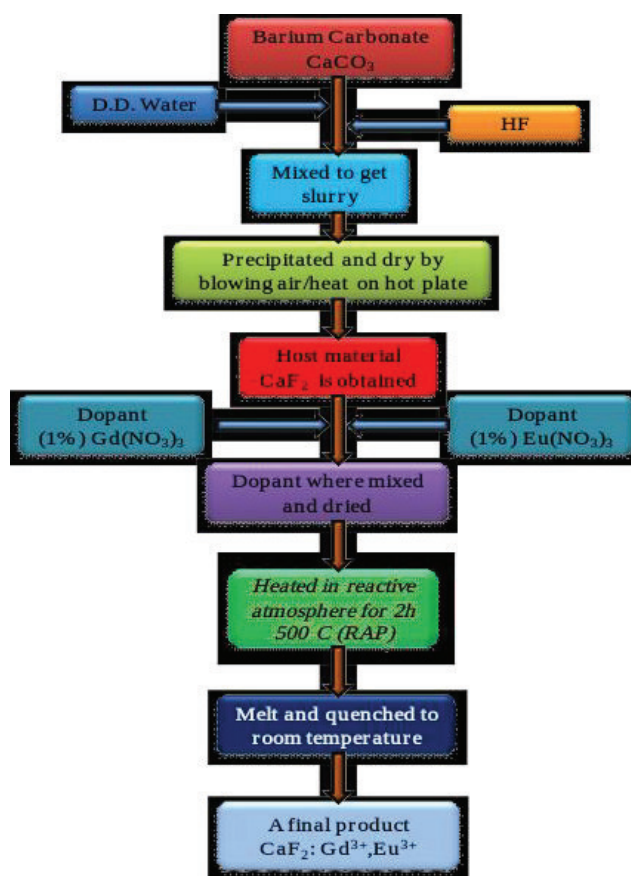


Fig.1. Flow chart of CaF<sub>2</sub>: Gd<sup>3+</sup>, Eu<sup>3+</sup> prepared via RAP.

## 3. RESULTS AND DISCUSSION

### 3.1 XRD Analysis

The formation of the CaF<sub>2</sub>: Gd<sup>3+</sup>, Eu<sup>3+</sup> sample in the crystalline phase synthesized by RAP was confirmed by XRD pattern as shown in Fig.2. The XRD pattern for CaF<sub>2</sub>:Gd<sup>3+</sup>, Eu<sup>3+</sup> agreed well with the standard data from ICDD file (00-004-0864). Also the XRD pattern show that CaF<sub>2</sub> lattice possesses cubic structure with a space group *Fm-3m* (225) with lattice parameters  $a = b = c = 5.2646 \text{ \AA}$  and interfacial angles  $\alpha = \beta = \gamma = 90^\circ$ . XRD pattern of CaF<sub>2</sub>:Gd<sup>3+</sup>, Eu<sup>3+</sup> phosphor as shown in fig.2.

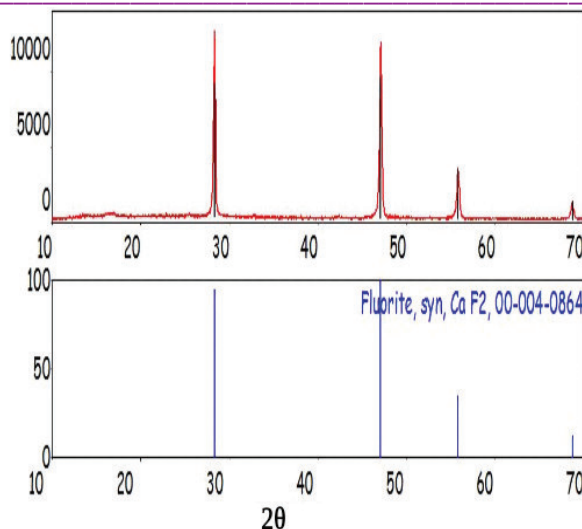


Fig.2.XRD patterns of CaF<sub>2</sub>: Gd<sup>3+</sup>, Eu<sup>3+</sup> synthesized by RAP.

### 3.2 VUV-UV PL Analysis

The emission spectra under excitation 274 and 203 nm are shown in Fig 4. 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>J</sub> (J=0, 1, 2, 3) →<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. There are broad excitations lines spectra peaking optimum at about 203, 227 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[8] as shown in Fig 3.

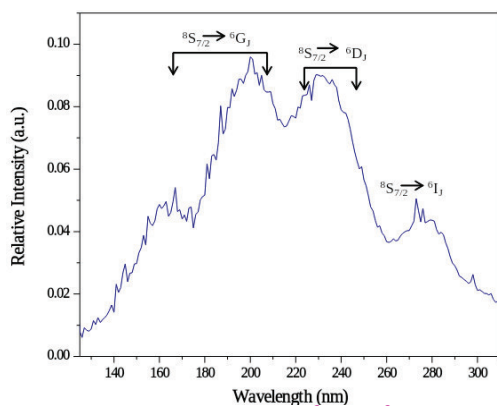


Fig.3.Excitation spectrum of CaF<sub>2</sub>: Gd<sup>3+</sup>, Eu<sup>3+</sup> monitored at 593 nm.

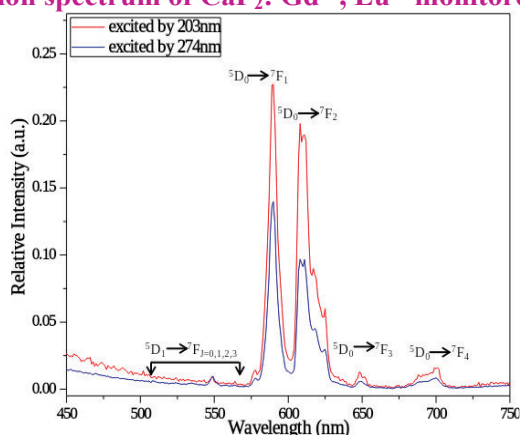
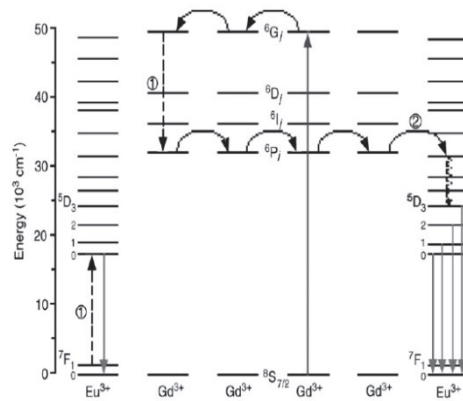


Fig.4.emission spectra of CaF<sub>2</sub>: Gd<sup>3+</sup>, Eu<sup>3+</sup> at excitation wavelength 203 and 274 nm.

The process transfer of energy and quantum splitting can happen by the combination of  $Gd^{3+}$  and  $Eu^{3+}$  in which  $Gd^{3+}$  and absorbing a VUV photon corresponding to  $^8S_{7/2} \rightarrow ^6G_J$ . The incident high energy photon is cut into two visible photons emitted by  $Eu^{3+}$  ions. The energy of transitions  $^6G_J \rightarrow ^6P_J$  on  $Gd^{3+}$  matches the  $^7F_J \rightarrow ^5D_0$  excitation energy on  $Eu^{3+}$ . Upon excitation in the  $^6G_J$  levels of  $Gd^{3+}$  as the first step, energy is transferred by cross-relaxation between  $Gd^{3+}$  and  $Eu^{3+}$  which make  $Gd^{3+}$  fall into the  $^6P_J$  state and  $Eu^{3+}$  is excited into the  $^5D_0$  state. The excited  $Eu^{3+}$  is responsible for the first visible photon. The first step is called as booming energy migration. In the second step the remaining excitation energy of  $Gd^{3+}$  in the  $^6P_J$  state is transferred to another nearing  $Eu^{3+}$  ion, i.e.  $Eu^{3+}$  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 the  $Eu^{3+}$  ion only excited into  $^5D_0$  state, only the emissions of  $^5D_0 \rightarrow ^7F_J$  transitions are expected. However after the second step, all levels of  $^5D_{3,2,1,0}$  of  $Eu^{3+}$  are probably engaged, so the emission wavelength consists of all of the  $^5D_J$  ( $J=0,1,2,3$ )  $\rightarrow ^7F_J$  transitions [9].



**Fig.5. Energy level diagrams of  $Eu^{3+}$  and  $Gd^{3+}$  showing the cross-relaxation energy transfer process that leads to quantum splitting [9, 10]**

Consecutively to calculate quantum efficiency, some assumption must be projected. The incident vacuum ultraviolet photon absorption efficiency cannot be taken into consideration. Some nonradiative losses at defects and impurities are disregarded. In the  $CaF_2:Gd^{3+}, Eu^{3+}$  sample, different excitations are adopted including the excitation of  $Gd^{3+} \rightarrow ^6G_J$  with 203 nm and the excitation of  $Gd^{3+} \rightarrow ^6I_J$  with 273 nm. Upon excitation in  $^6I_J$  level with 273 nm, the quantum cutting never occurs because no cross-relaxation exists, so the  $^5D_J \rightarrow ^7F_J$  transitions emission of  $Eu^{3+}$  has a normal branching ratio between  $^5D_0$  and  $^5D_{1,2,3}$ . Upon 203 nm excitation in  $^6G_J$  level with, the quantum cutting can occur via two-step energy transfer. In the second step, the emission of  $Eu^{3+}$  has a normal branching ratio. The first step will pilot 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:

$$\frac{P_{CR}}{P_{CR} + P_{DT}} \approx \frac{R(^5D_0/^5D_{1,2,3})_{6G_J} \times R(^5D_0/^5D_{1,2,3})_{6I_J}}{R(^5D_0/^5D_{1,2,3})_{6I_J} + 1}$$

Where  $P_{CR}$  is the probability for cross-relaxation,  $P_{DT}$  is the probability for the direct transfer from  $Gd^{3+}$  to  $Eu^{3+}$ .  $R(^5D_0/^5D_{1,2,3})$  is the ratio of the  $^5D_0$  and  $^5D_{1,2,3}$  emission integral intensities. The subscript ( $^6G_J$  or  $^6I_J$ ) represents the excitation level for which the ratio is observed. From the emission spectra, the value of  $R(^5D_0/^5D_{1,2,3})_{6G_J}$  and  $R(^5D_0/^5D_{1,2,3})_{6I_J}$  can be calculated 33.21 and 27.15, respectively. Therefore, the value of  $P_{CR}/P_{CR} + P_{DT}$  is 0.17. It means that there are 17%  $Gd^{3+}$  ions in the  $^6G_J$  excited state settle down through a two-step energy transfer emitting two visible photons in this method. So the quantum cutting efficiency of 117% can be obtained. Quantum cutting in the Gd to Eu understanding requires energy transfer over the Gd sublattice to Eu [10].

#### 4. CONCLUSIONS

The inorganic material  $\text{CaF}_2: \text{Gd}^{3+}, \text{Eu}^{3+}$  was successfully prepared through reactive atmosphere process. The XRD pattern confirmed its cubic structure. The visible quantum cutting and energy transfer through down-conversion was observed in  $\text{CaF}_2: 1\% \text{Gd}^{3+}, 1\% \text{Eu}^{3+}$  and the quantum efficiency was found to be around 117% under the excitation of 203 nm equivalent  $^8\text{S}_{7/2} \rightarrow ^6\text{G}_7$  transition of  $\text{Gd}^{3+}$  ions.

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