VUV SPECTRAL PROPERTIES OF Gd^{3+}, Eu^{3+} IONS PAIR DOPED $LiBaF_3$ PHOSPHOR SYNTHESIS VIA WET CHEMICAL METHOD.

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Abstract: The novel gadolinium, europium doped, and co-doped Lithium Barium Fluoride were successfully synthesized by a low-cost and time-saving wet chemical method followed by Reactive Atmosphere Process (RAP). The purity of phase was checked by X-ray powder diffraction technique (XRD). The luminescent properties in ultraviolet or vacuum ultraviolet (UV-VUV) region were first time examined in the synthesized $LiBaF_3$: Gd^{3+}, Eu^{3+} Phosphor. The excitation spectra in VUV region (from 125 to 300 nm) were recorded at a 618 nm emission wavelength. Strong photoluminescence emission spectra were attained at 593, 618, and 627 nm at excitation wavelength 252 nm. The photoluminescence emission spectra are related with the transition from excited $^5D_0$ level to the ^7F_J (J = 1, 2, 3, 4) levels of Eu^{3+} activators. The visible quantum cutting (QC) via down-conversion (DC) has been observed in $LiBaF_3$: Gd^{3+}, Eu^{3+} phosphor. The process of cross relaxation energy transfer (CRET) very minutely was observed in Gd^{3+}- Eu^{3+} ions pair doped with host $LiBaF_3$. As per the calculation from emission spectra monitor at 252 nm excitation wavelength, we can obtain two step energy transfer process with a visible QC of up just greater than unity. In the synthesis phosphor we got the value of quantum efficiency (QE) 100.7%.

Index Terms – Visible Quantum Cutting, Down Conversion, Quantum Efficiency, Mercury Free Fluorescent Lamp (MFFL)

1. INTRODUCTION

Luminescent Materials with lanthanide are found in, x-ray photography, colour TV, laser, up-conversion materials that convert infrared (IR) to visible light, fiber amplifiers, and fluorescent tubes [1-3]. Th luminescent properties of lanthanide ions (high efficiency and sharp line) are responsible for such type of application. The Hg-discharge white light fluorescent tubes (λex = 254 nm in UV region) were replaced with a noble gas, such as mercury-free (Hg-free) Xe-discharge fluorescent tubes (λex = 147 & 172 nm in VUV region) due to the environmental issues and low quantum efficiency. But some others disadvantages were founded in the Xe-discharge fluorescent tube over Hg-based fluorescent lamps. The disadvantages are, that the low luminescence efficacy of xenon discharge lamp and Most of the energy (65%) loss is due to the non-radiative relaxation process from VUV photon as compared to Hg-based fluorescent lamps (FL) (losses of 50%). Therefore, we need to reduce the higher energy loss and achieve the QE of the phosphors by greater than unity (100%) in Xe-discharge FL. In theory, this is conceivable only when the emission of two visible photons per each absorbs a high energy VUV photon that generate in a noble gas discharge.

The researcher found the visible QC is possible with the Gd^{3+} - Eu^{3+}/Tb^{3+} ions couple doped in many fluoride host materials such as BaF_2 [4], $LiGdF_4$ [5], K_2GdF_5 [6], $BaYF_5$ [7] and many more.

Motivated by the few reported fluoride-based quantum cutting (QC) phosphors, we have investigated the phosphor LiBaF$_3$ doped with Gd^{3+} - Eu^{3+} rare-earth ions couple. Here with produced a statement that, the QC process of a novel red light emitting phosphor prepared by the wet chemical followed by RAP method. The crystal stature was established using powder XRD. We can obtain the two-step energy transfer process from the emission spectra under 252 nm excitation wavelength with a visible quantum efficiency greater than 100%.

2. EXPERIMENTAL

The phosphor LiBaF$_3$: Gd^{3+}, Eu^{3+} was the first time prepared by wet chemical method followed by RAP; which contributed to a relatively hight controllability, low temperature, time saving, and low cost are the main advantages. The starting chemical Lithium Nitrate (LiNO$_3$) (99.99% A.R.), and Barium carbonate BaCO$_3$ (99.99% A.R.) are used as precursors, and Gadolinium Oxide (Gd$_2$O$_3$) (Loba 99.9%) and Europium Oxide (Eu$_2$O$_3$) (Loba 99.9%) are used as a dopant. The precursors and dopant were taken in a Teflon beaker and dissolved in the least amount of HNO$_3$. The solution was heated to 100 °C and dried completely to get an aqueous solution of LiBa (NO$_3$)$_3$: Gd, Eu. By adding 20 ml of double distilled (DD) water to the solution and stirring, hydrofluoric acid (HF) was added dropwise to get white precipitated. The precipitate was washed and filtered then heated on a hot plate (80°C) to get dried white powder.

The dry precipitate was shifted 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 1 h. The stopper was removed and the powders were transferred to a pre-heated graphite crucible heat to an 800 °C temperature for 1 hour. The resulting phosphor was rapidly quenched to room temperature. Belsare *et al.* & Jaiswal *et al.* was well-discussed RAP in their literature [8-10]. The complete process involved in the reaction was represented as a flow chart in Fig. 1.
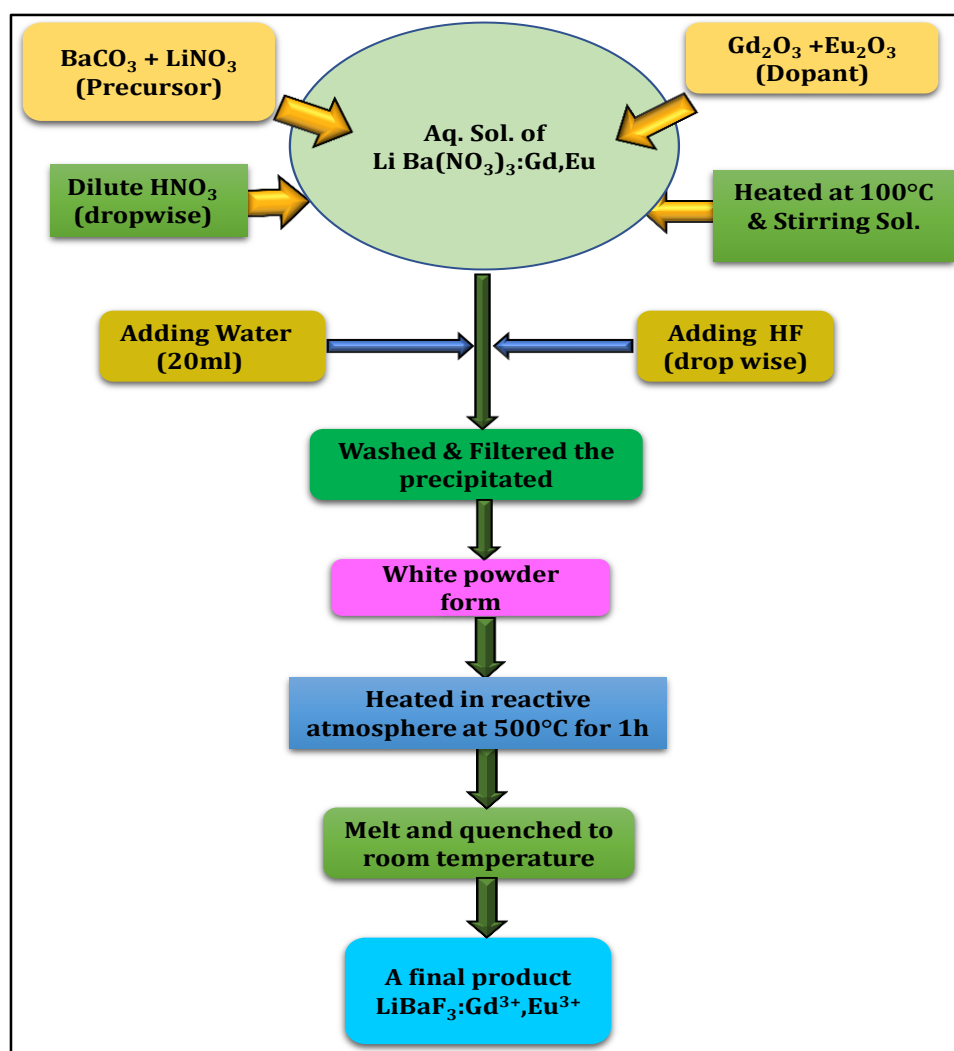

Fig. 1. Flow chart represented the complete process involved in the reaction

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

The X-ray diffraction (XRD) pattern of samples (host with dopant) was recorded on Rigaku MiniFlex diffractometer with a scan speed of 2000 deg/min. The XRD pattern for $LiBaF_3$: Gd^{3+}, Eu^{3+} agreed well with the standard data from the ICDD file (01-073-6641) as shown in Fig.2. The peaks from the XRD pattern of phosphor prepared by the wet chemical method form at 22.25, 31.67, 39.05, 45.40, 51.12, and 56.41 corresponding to (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0) and (2 1 1) respectively, show exact matching with standard ICDD file data. Also, the XRD pattern shows that $LiBaF_3$ lattice possesses a cubic structure with a space group Pm-3m (221) with lattice parameters a = b = c = 3.9920 A° and interfacial angles α = β = γ = 90°.
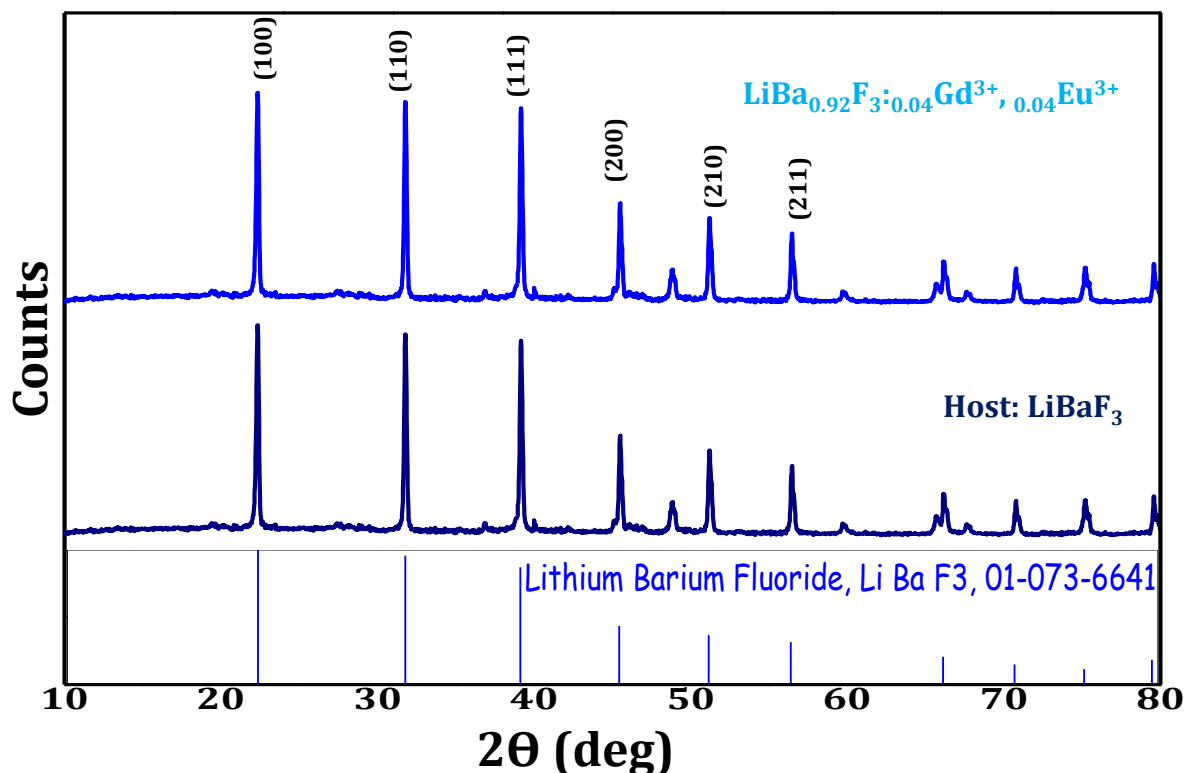

Fig. 2. XRD pattern of the synthesized $LiBaF_3$ doped and undoped material

3.2 Studies of Photoluminescence Spectra

First, we investigated the concentration quenching of Gd^{3+} as a sensitizer in the $LiBaF_3$ host. From Fig.3 it can be stimulated that at 4 mol% of Gd^{3+} ions in the $LiBaF_3$ host, it shows an optimal intensity peak at 311/312 nm under the excitation of 274 nm.
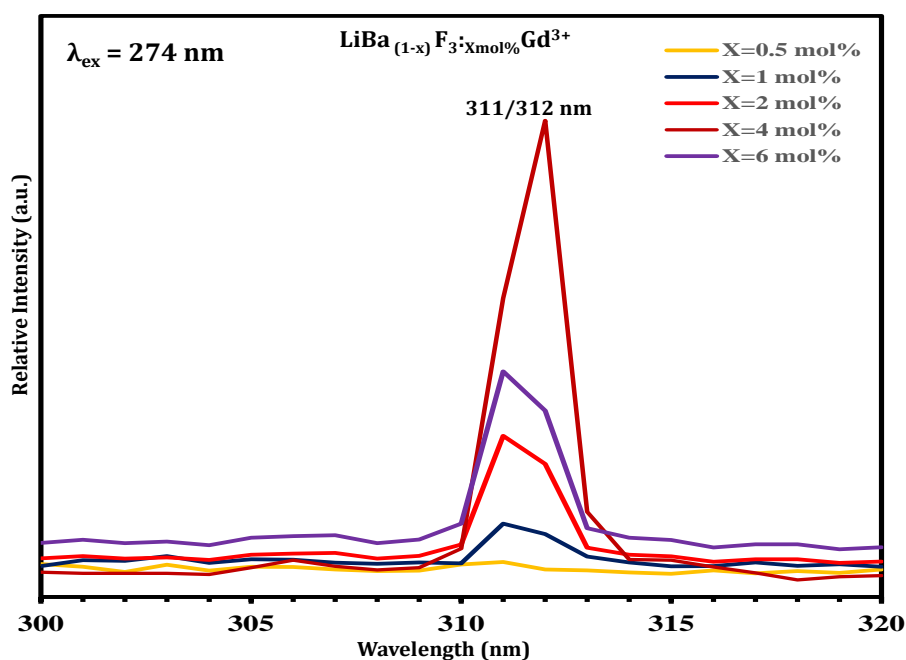

Fig. 3. Emission spectra of $LiBaF_3$ host doped Gd^{3+} as a sensitizer monitored at 274 nm

The photoluminescence excitation and emission spectra in the VUV-UV range using synchrotron radiations for $LiBa_{(0.96-X)}F_3:_{0.4mol\%}Gd^{3+},\ _{X\ mol\%}Eu^{3+}$ ($0.05 \le X \le 0.4$) phosphors were studied:

3.2.1. Excitation spectra

The excitation spectrum with an emission wavelength of 618 nm is shown in Fig. 4.
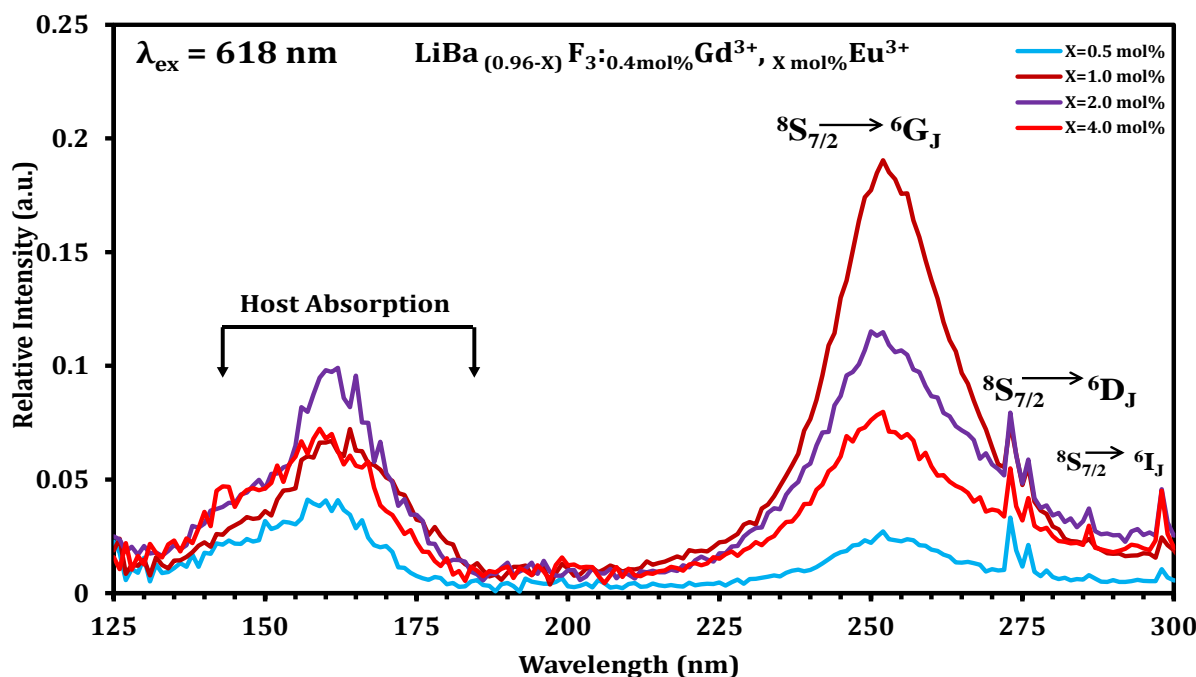

Fig. 4. Excitation spectrum of $LiBa_{(0.96-X)}F_3:_{0.4mol\%}Gd^{3+},\ _{X\ mol\%}Eu^{3+}$ ($0.05 \le X \le 0.4$) phosphors monitored at 618 nm.

There are two main broad excitation peaks observed in the excitation spectra. One is ascribed to absorption of the host lattice in the range 130 - 185 nm, maximum at 164 nm, and the second excitation peaks are attributed to excitation lines peaking at about 252, 274, 285, and 298 nm responsible for $^8S_{7/2} \to ^6G_J$, ^6D_J, and ^6I_J respectively of Gd^{3+}. The oxygen ions easily substitute for fluoride ions, degrading the optical

presentation of fluoride phosphors. The oxygen impurities may be easily detected in the case of Eu^{3+}-doped materials since their presence gives rise to an intense $O^{2-} \rightarrow Eu^{3+}$ charge transfer band observed at approximately 252 nm [11].

3.2.2. Emission spectra

Figure 5 shows the emission spectra of $LiBa_{(0.96-X)}F_3{:}_{0.4mol\%}Gd^{3+},\ _{X\ mol\%}Eu^{3+}\ (0.05 \leq X \leq 0.4)$ in the range of 450-750 nm under the excitation wavelength 252 nm. The emission lines of Eu^{3+} peaked at about 593, 618, 650, and 700 nm corresponding to $^5D_0 \rightarrow {}^7F_J$ (J=1, 2, 3, 4) transitions respectively, and the $^5D_1 \rightarrow {}^7F_{J=0,1,2,3}$ transition peaks of Eu^{3+} are much weaker than those of $^5D_0 \rightarrow {}^7F_J$ transition are shown in figure 5.
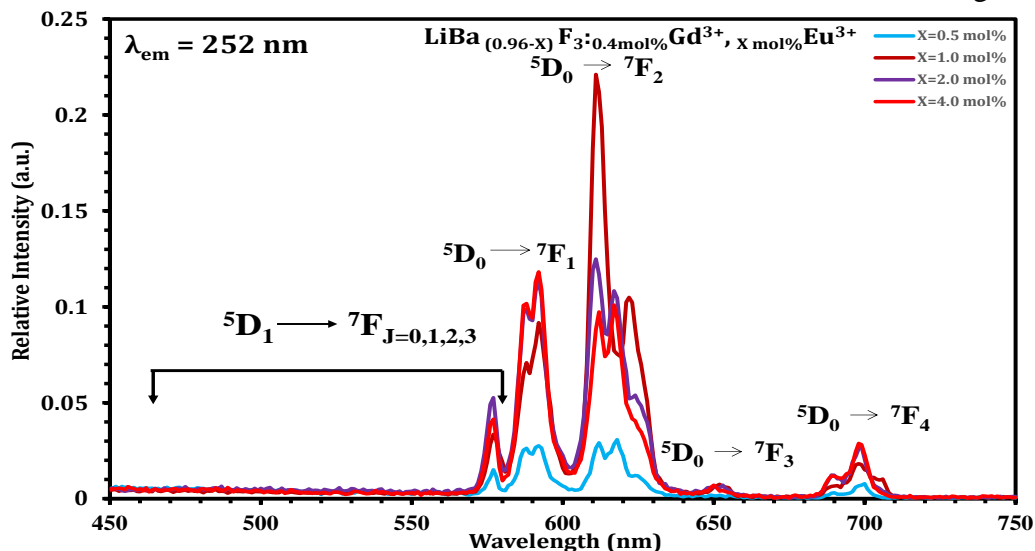

Fig 5: Emission spectra of $LiBa_{(0.96-X)}F_3{:}_{0.4mol\%}Gd^{3+},\ _{X\ mol\%}Eu^{3+}\ (0.05 \leq X \leq 0.4)$ under the excitation wavelength 252 nm.

3.2.3 Energy transfer and quantum cutting

Figure 6 represents the photoluminescence emission spectra of $LiBa_{0.95}F_3{:}_{0.4\ mol\%}Gd^{3+},\ _{1.0\ mol\%}Eu^{3+}$ in the range of 450-750 nm monitored by 164, 252, and 274 nm respectively for the study of quantum efficiency and energy transfer process.
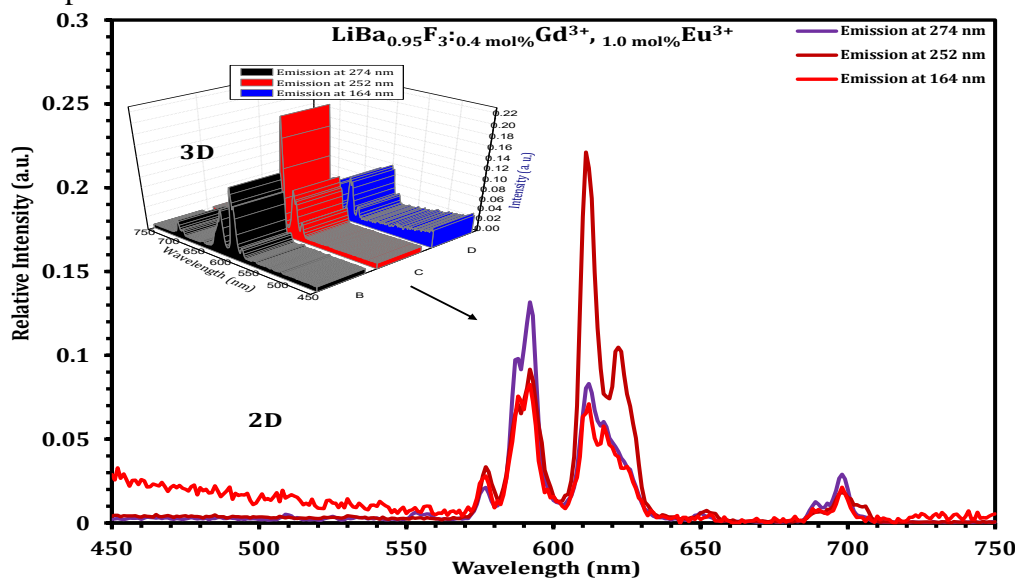

Fig 6: The PL emission spectra of $LiBa_{0.95}F_3{:}_{0.4\ mol\%}Gd^{3+},\ _{1.0\ mol\%}Eu^{3+}$ monitored at 164, 252, and 274 nm

With the help of Ref. [12], we try to find the occurrence of energy transfer and find the quantum efficiency of synthesized phosphor. Thus, a comparison of the $^5D_0/^5D_{1,2,3}$ emission intensity ratio upon exciting in $Gd^{3+}\ ^6G_J$ and ^6P_J (or ^6I_J, ^6D_J) levels may be used for the calculation of the efficiency of the CR step. we have calculated the extra QE used by the equation proposed by Wegh et al. [12-18]

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

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 $^5D_0$ and $^5D_{1,2,3}$ emission integral intensities ratio. The subscript (^6G_J or ^6I_J) represents the excitation level for which the ratio is observed. From the emission spectra, at the excitation wavelengths 252, and 274 nm, the value of R ($^5D_0/^5D_{1,2,3})^6G_J$ and ($^5D_0/^5D_{1,2,3})^6I_J$ can be calculated at 6.1380 and 5.6300, respectively. Therefore, the value of $P_{CR}/P_{CR} + P_{DT}$ is 0.07. It means that there are very minute i.e. 0.7% 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, a quantum cutting efficiency of 100.7% can be obtained.

4. CONCLUSIONS

The inorganic material $LiBaF_3$: Gd^{3+}, Eu^{3+} was successfully prepared through a wet chemical method followed by a reactive atmosphere process. The XRD pattern confirmed its cubic structure. The visible quantum cutting and energy transfer through down-conversion were observed very minutely i.e., 100.7% in $LiBaF_3$: Gd^{3+}, Eu^{3+} at the excitation wavelength 252 nm, and quantum efficiency less than unity was found at 164 nm excitation.

5. ACKNOWLEDGMENTS

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