International Journal of Scientific Research in Science and Technology
Print ISSN: 2395-6011 | Online ISSN: 2395-602X (www.ijsrst.com)
© 2021 | IJSRST | Volume 8 - Issue 1

Energy Transfer Process in MgF_2 : Gd^{3+}, Eu^{3+} Phosphor : Application to Visible Quantum Cutting

S. R. Jaiswal*[1], P. A. Nagpure[2], S. K. Omanwar[3]

[1*] Department of Physics, Shri R.L.T. College of Science, Akola, Maharashtra, India

[2]Department of Physics, ShriShivaji Science College, Amravati, Maharashtra, India

[3]Department of Physics, SantGadge Baba Amravati University, Amravati, Maharashtra, India

ABSTRACT

Visible quantum cutting (QC) is observed in MgF_2 Co-doped with Gd^3, Eu^{3+} phosphor synthesis via wet chemical method. Powder X-ray diffraction analysis shows structural purity. The emission and excitation spectra of MgF_2:Gd^{3+}, Eu^{3+} were investigated using the VUV beam line of the Beijing Synchrotron Radiation Facility (BSRF). Energy transfer in gadolinium compounds from the Gd^{3+} ions to Eu^{3+} through cross relaxation occurs in this process. Quantum efficiency was found to be greater than 100% under the excitation of 172 nm and 203 nm corresponding $^8S_{7/2}$ ^6G_J transition of Gd^{3+} ions. The synthesized phosphor material is potential candidates for the applications of plasma display panel and mercury free fluoresce lamps.

Keywords : Quantum Cutting, Plasma Display Panels (PDPs), VUV Spectroscopy

I. INTRODUCTION

For the development of mercury free florescent 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. [3-6]

II. METHODS AND MATERIAL

MgF_2: Gd^{3+}, Eu^{3+} phosphor was synthesis via reactive atmospheric process. In this method we used metal carbonate like $MgCO_3$(99.99% A.R.) as a precursor. The inorganic magnesium carbonate was taken in Teflon beaker. A little amount of double distilled water was added in beaker and stired 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 MgF_2 host was obtained. Gd_2O_3 (AR 99.9%) and Eu_2O_3 (AR 99.9%) were boiled in HNO_3 and evaporated to dryness, so as to convert them into relevant nitrates. The aqueous

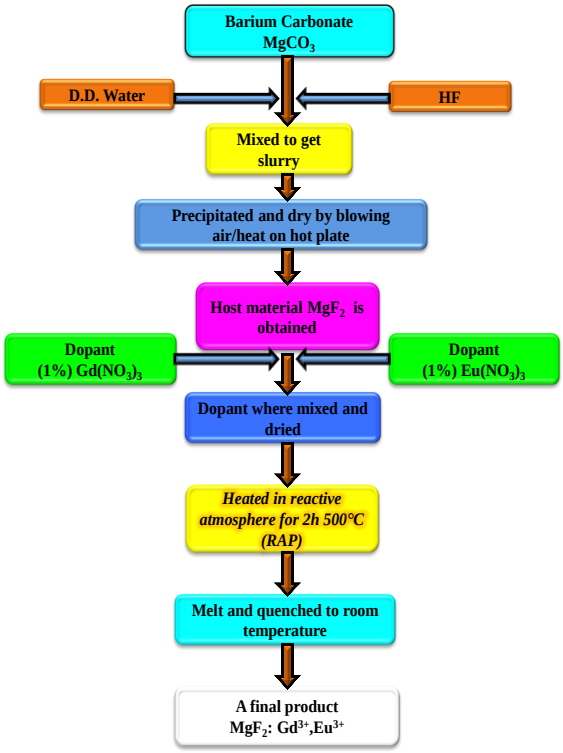
solution of these nitrates where use as a dopants. The 1 mol% of gadolinium nitrate and 1mol% of europium nitrate where assorted in the host material and dehydrated completely.

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.

III. RESULTS AND DISCUSSION

3.1 XRD Analysis

The formation of the MgF_2: Gd^{3+}, Eu^{3+}sample in the crystalline phase synthesized by RAP was confirmed by XRD pattern as shown in Fig.2. The XRD pattern for MgF_2:Gd^{3+}, Eu^{3+} agreed well with the standard data from ICDD file (01-070-8282). Also the XRD pattern show that MgF_2 lattice possesses Tetragonal structure with a space group *P42/mnm(136)*with lattice parameters *a =b=4.5964 A° and c= 3.0376 A°* and interfacial angles $\alpha = \beta = \gamma = 90°$. XRD pattern of MgF_2:Gd^{3+}, Eu^{3+} phosphor as shown in fig.1.



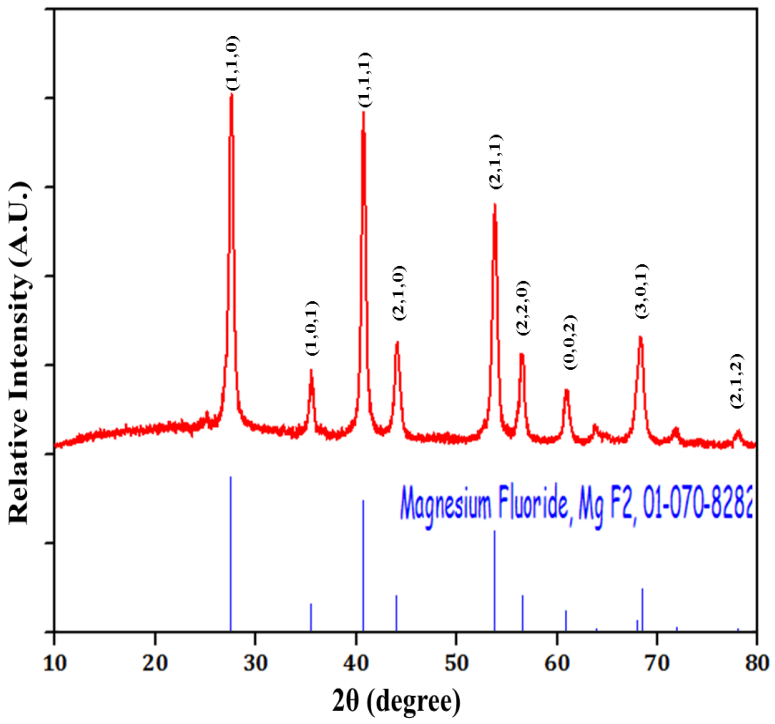


Fig.1 Fig.2

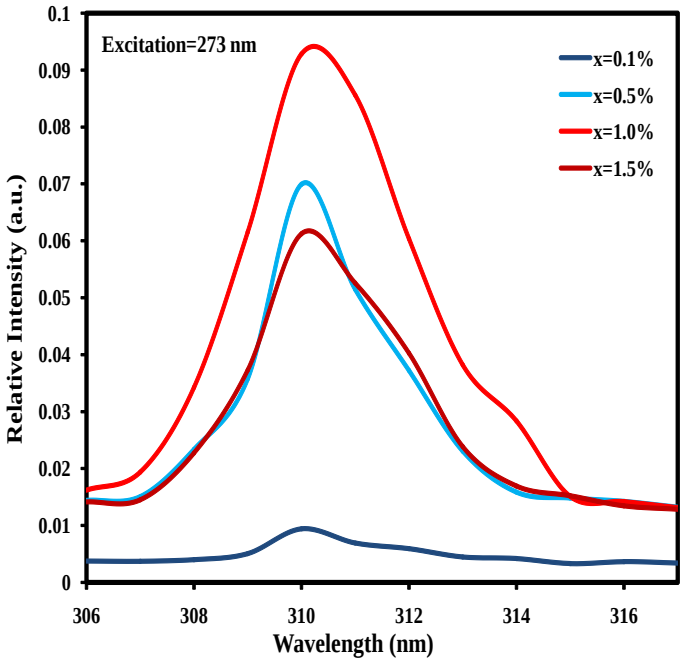
Fig.1. Flow chart of MgF_2: Gd^{3+}, Eu^{3+} prepared via RAP.

Fig.2.XRD patterns of MgF_2: Gd^{3+}, Eu^{3+} synthesized by RAP.

3.2 VUV-UV PL Analysis

The concentration quenching of Gd^{3+} as a sensitizer in MgF_2 host background was resolute. From the Fig.3 it can be encouraged that at 1 mol% of Gd^{3+} ions in MgF_3 host shows optimum intensity peak at 311 nm under the excitation of 273 nm. The emission spectra under excitation 273 and 203 nm are shown in Fig 5. The emission lines of Eu^{3+} peaked at about 593, 613, 650 and 700nm correspond to $^5D_0 \rightarrow {}^7F_J$ (J=1, 2, 3, 4) transitions respectively and the ^5D_J (J=0, 1, 2, 3) $\rightarrow {}^7F_J$ transition peaks of Eu^{3+} are much weaker than those of $^5D_0 \rightarrow {}^7F_J$ transition. There are broad excitations lines spectra peaking optimum at about 203, 227 and 274 nm responsible for $^8S_{7/2} \rightarrow {}^6G_J$, ^6D_J, ^6I_J respectively [8] as shown in Fig 4.

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].



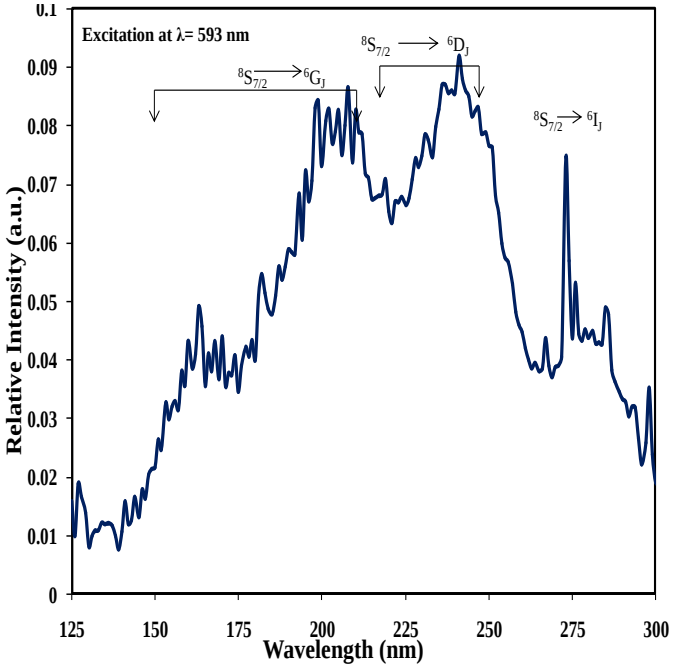
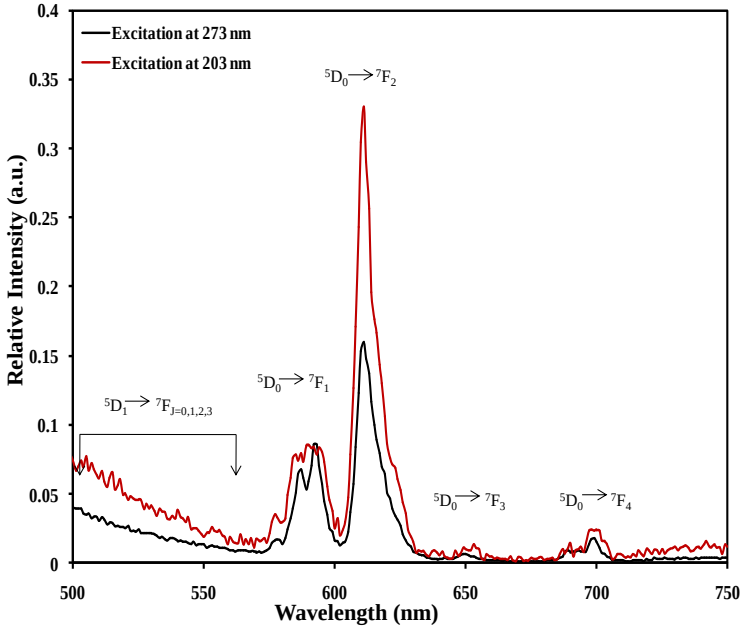


Fig.3 **Fig.4**

Fig.3.Emission spectra of MgF_2: X%Gd^{3+} under the excitation of 273 nm.

Fig.4.Excitation spectrum of MgF_2: Gd^{3+}, Eu^{3+} monitored at 593 nm.



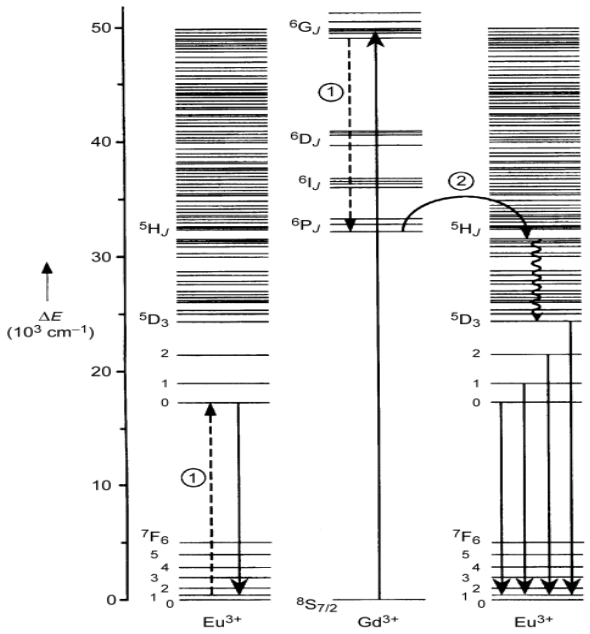


Fig.5 **Fig.6**

Fig.5.Emission spectra of MgF_2: Gd^{3+}, Eu^{3+} at excitation wavelength 203 and 274 nm.

Fig.6.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 MgF_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 [11-20] was adopted as follows:

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

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 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 ($^5D_0/^5D_{1,2,3}$)^6I_J can be calculated 44.12 and 29.42, respectively. Therefore, the value of $P_{CR}/P_{CR} + P_{DT}$ is 0.32. It means that there are 32% 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 132% can be obtained. Quantum cutting in the Gd to Eu understanding requires energy transfer over the Gdsublattice to Eu [10].

IV. CONCLUSION

The inorganic material MgF_2: Gd^{3+}, 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 MgF_2:1% Gd^{3+}, 1% Eu^{3+} and the quantum efficiency was found to be around 132% under the excitation of 203 nm equivalent $^8S_{7/2} \rightarrow {}^6G_J$ transition of Gd^{3+} ions.

V. ACKNOWLEDGEMENTS

We are thankful to 4B8 VUV spectroscopy beam line scientists of Being Synchrotron Radiation Facility (BSRF), China for given that access in recording VUV on beamline 4B8 under dedicated synchrotron mode using remote access mode. One of the authors S.R. Jaiswal thankful to Head, Department of Physics SantGadge Baba Amravati University, Amravati for providing necessary facilities.

VI. REFERENCES

[1]. C.R. Ronda, J. Alloys Compd. 225 (1993) 534.

[2]. M. Y. William, Phosphor Handbook, CRC press is an imprint of the Taylor & Francis Group, ISBN: 0-8493-3564-7.

[3]. S. Pote, C. Joshi, S. Moharil, P. Muthal, S. Dhopte. ISSN 1061-3862, International Journal of Self- Propogating High-Temperature Synthesis. 22 (2013) 37-40

[4]. B. Herden, A. García-Fuente, H. Ramanantoanina, T. Jüstel, C. Daul, W. Urland, Chemical physics letter. 620 (2015) 29-34.

[5]. W. Binder, S. Dislerhoff, J. Cameron, Dosimetric Properties of CaF2: Dy, (a) Proc. II Int. Conf. on Lumin. Dosim.,Gatlinberg, 1968, pp. 45–53; (b) Health Phys., 1969, vol. 17, no. 4, pp. 613–618.

[6]. (a) A.C. Lucas, R.H. Moss, B.M. Casper, Thermoluminescent CaF2:Tm and Method for Its Use, US Patent 4 039 834, 1977; (b) Lucas, A.C. and Casper, B.M., Thermoluminescence of Thulium Doped Calcium Fluoride, Proc. Int. Conf. on Lumin. Dosim., Sao Paulo (Brazil), 1977, pp. 131-139

[7]. P. Belsare, C. Joshi, S. Moharil, V. Kondawar, P.Muthal, S. Dhopte, J. Alloys Compd. 450 (2008) 468–472.

[8]. R.T. Wegh, E.V.D. van Loef, A. Meijerink , J. Lumin., 90 (2000) 111.

[9]. B. Liua, Y. Chena, C. Shia, H. Tanga, Y. Tao, Journal of Luminescence 101 (2003) 155–159.

[10]. R.T. Wegh, H. Donker, K. Oskam, and A. Meijerink, J. Lumin., 82 (1999) 93.

[11]. R.T. Wegh, H. Donker, K. Oskam, A. Meijerink, Science 663 (1999) 283.

[12]. N. Kodama, Y. Watanabe, Appl. Phys. Lett. 4141 (2004) 84.

[13]. N. Kodama, S. Oishi, J. Appl. Phys. 103515 (2005) 98.

[14]. R. Hua1, J.H. Niu, B.J. Chen, M.T.Z. Li, T. Yu, W.L. Li, Nanotechnology 1642 (2006) 17.

[15]. Y. Zhou, S.P. Feofilov, J.Y. Jeong, D.A. Keszler,R.S. Meltzer, Phys. Rev. B 075129 (2008) 77.

[16]. M. Karbowiak, A. Mech, W. Ryba-Romanowski, J. Lumin. 65 (2005) 114.

[17]. B. Liu, Y.H. Chen, C.S. Shi, H.G. Tang, Y. Tao, J. Lumin. 101 (2003) 155.

[18]. S.K. Omanwar, S.R. Jaiswal, P.A. Nagpure, V. B. Bhatkar, J. Material Sci.: Material in Electronic(2016) 1-8

[19]. S.K. Omanwar, S.R. Jaiswal, N.S. Sawal, K.A. KoparkarP.A.Nagpure, V. B. Bhatkar, St. petrbergpolytechenicaluniversityJournal : Physics and mathematics 3 (2017) 218-224.

[20]. S.R. Jaiswal, N.S. Sawal, K.A. Koparkar, V. B. Bhatkar, S.K. Omanwar, material discovery, 7 (2017) 15-20.