Orange/Red Luminescence Properties of $K_2CaMg(SO_4)_3$: Eu^{3+} Phosphor

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***Abstract*— The phosphors Eu^{3+} activated $K_2CaMg(SO_4)_3$ were prepared by wet-chemical method. Study of X-Ray diffraction and SEM micrographs were used to determine their phase formation, purity and morphology. Photoluminescence properties were measured at room temperature. The results revealed that the $K_2CaMg(SO_4)_3$: Eu^{3+} phosphors can be effectively excited by near-UV (393nm) light and exhibit two prominent emission bands peaked at 593 nm and 613 nm contribute to the orange-red emission. The concentration quenching mechanism was verified as exchange interaction. The change in concentration of Mg in the host affect the photoluminescence characteristics of $K_2CaMg(SO_4)_3$.**

***Keywords*— $K_2CaMg(SO_4)_3$; wet chemical method; XRD; SEM; Photoluminescence.**

I. INTRODUCTION

There are many applications of luminescent materials such as colour display, scintillators, fluorescent lamps, intensifying screens, dosimetry of ionizing radiations and so on [1]. Lanthanides are usually doped in these materials as divalent or trivalent cations to activate the host materials for photonic and optoelectronic applications. Many researchers have been reported that the mixed sulphate phosphors can be used as dosimeters of ionizing radiations [2-4]. Due to having well-desired characteristics like a high-temperature glow peak, linear response with ionizing radiation exposure, low fading and an easy method of preparation, mixed sulphate phosphors have a great importance. Deshpande et al studied photoluminescence (PL) and thermoluminescence (TL) characteristics of $K_2Mg(SO_4)_2$:Dy and also were evaluated the trapping parameters [5]. Sahare and co-workers reported the PL and TL characteristics of rare earth doped $K_2Ca_2(SO_4)_3$ nanocrystalline phosphor and observed the effect of phase transition, particle size, sensitivity etc [6-10]. Mixed sulphates show good performances, especially when doped with proper activators [11, 12]. Some of the phosphors like $KMgSO_4Cl$: Eu, Ce halosulphate and $Na_5(PO_4)SO_4$:Ce phosphate sulphate phosphors reported for the application of scintillation purposes [13, 14]. Blasé et al [15-17] studied Eu^{3+} emission extensively in various hosts for white light-emitting diodes (WLED). WLED are potential replacement for incandescent and fluorescent light sources because of their high luminous efficiency, low cost synthesis, energy saving, long lifetime, and environmental protection. Kore et al studied [18] TL and EPR study of Dy^{3+} doped triple sulphate $K_2CaMg(SO_4)_3$ phosphors and reported the energy levels, wave functions and the interactions of all the multiplets of the $^4f_9$ configuration.

In this work, first time we have reported synthesis and photoluminescence characteristics of Eu^{3+} ions in $K_2CaMg(SO_4)_3$ phosphors. The PL emission spectrum of phosphors under near UV excitation shows an intense Eu^{3+} emission in the orange/red region.

II. MATERIALS AND METHOD

The samples were prepared by wet chemical method. While preparing $K_2CaMg(SO_4)_3$, the raw materials like potassium sulphate $[K_2(SO_4)H_2O]$, calcium sulphate $[Ca(SO_4)H_2O]$, Magnesium sulphate $[Mg(SO_4).7H_2O]$, and rare earths europium oxide $[Eu_2O_3]$, all A.R. grade were taken in a stoichiometric ratio.

$$K_2(SO_4)H_2O + Ca(SO_4H_2O + Mg(SO_4).7H_2O + x\ Eu_2O_3 \rightarrow K_2CaMg(SO_4)_3{:}\ xEu \qquad \text{--------}\ (1)$$

The samples were prepared in two steps. Initially, above all the raw materials in stoichiometric amounts were taken in separate beakers and dissolved in double distilled de-ionized water so that their transparent solutions were obtained. Similarly dopant material Eu_2O_3 was also dissolved in double distilled de-ionized water in a separate beaker. Then all the transparent solutions were added together to obtain a homogeneous solution of $K_2CaMg(SO_4)_3$: Eu. The resultant solution was stirred using a magnetic stirrer for >30 min. It was confirmed that no undissolved constituents were left behind in the solution and all the salts were completely dissolved in water. A series of Eu^{3+} doped phosphors was prepared for different concentrations (0.5, 1, 1.5, and 2 mol %). The sample in its powder form was obtained by evaporating at 80 °C for 8 h. The dried sample was then crushed and quenched at 700°C for 1 hr, where the redox reaction occurs. The resultant powder was taken out of the furnace and crushed to fine powder using an agate pestle and mortar. This powder was used as a phosphor in further study.

III. RESULTS AND DISCUSSION

A. Phase identification and morphology

The XRD patterns of $K_2Ca_{2-X}\ Mg_X(SO_4)_3$ for different (x) values are shown in Fig.1. The crystallite size of $K_2Ca_{2-X}\ Mg_X(SO_4)_3$ phosphors with different (x) values can be calculated from the broadening of strong peaks. The average structural particle size was estimated from the full width at half maximum of the diffraction peak by the Scherer formula.

$$D = k\ \lambda/\beta \cos\theta \qquad \text{--------}\ (2)$$

Where D is the mean crystallite diameter, k = 0.9 is the Scherer constant, λ is the X-ray wavelength (1.54 Å), and β is the full width half maximum (FWHM) of $K_2CaMg(SO_4)_3$ diffraction peak. The average crystallite size calculated using the most intense peaks and found to be 75.58 nm. It can be seen that all the samples have the orthorhombic crystal structure (nalipoite).

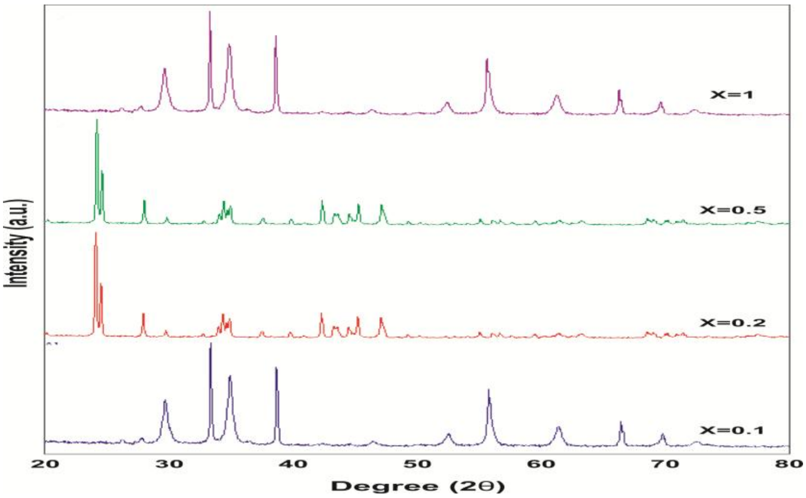

Fig.1 XRD pattern of $K_2Ca_{2-X}\ Mg_X(SO_4)_3$ with different content of Mg (x)

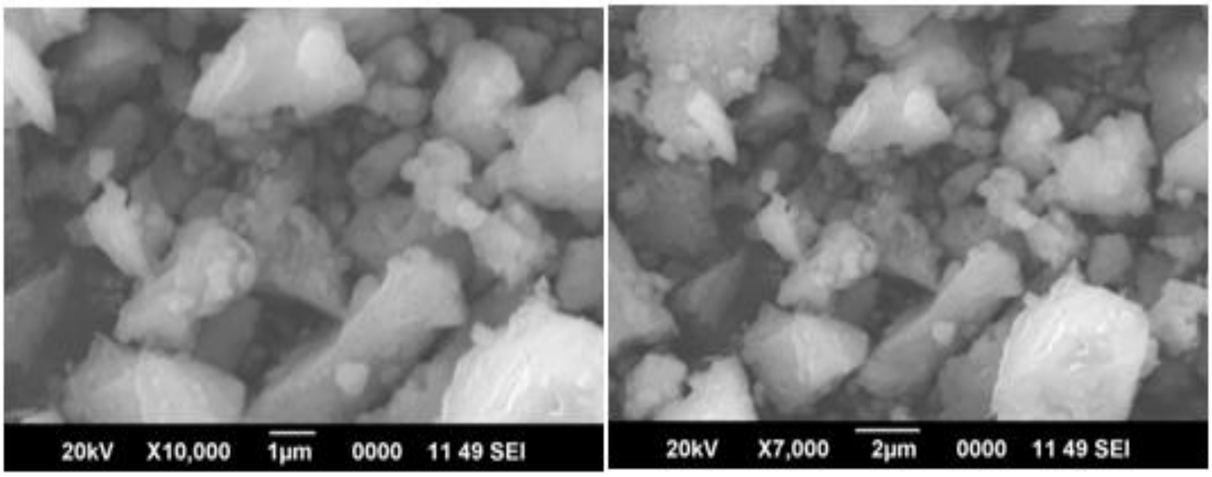

Fig. 2 SEM images of $K_2CaMg(SO_4)_3$ phosphor.

The typical morphological image of $K_2CaMg(SO_4)_3$ are represented in Fig.2. It is clearly seen that the grains have an irregular shape of particles with a size less than 1μm. This shows that the wet chemical reactions of the mixtures took place well. The particles possess rectangular foamy like shape formed from highly agglomerated crystallites. An average crystallite size is in nanometer range and formation of spongy cottons type structure is seen in SEM image. This indicates that this experimental processing is favourable for the crystalline growth of Buchwaldite type crystal structure.

B. Photoluminescence studies

The Photoluminescence excitation and emission spectra of $K_2CaMg(SO_4)_3$: Eu^{3+} are illustrated in Fig.3. The photoluminescence excitation spectrum shows a sharp peak at 393nm, monitored at 593nm emission wavelength. The narrow excitation lines appeared at longer wavelength corresponds to the characteristics f-f transition of Eu^{3+}, which is assigned to $^7F_0 \rightarrow {}^5L_6$ (393nm) transition of Eu^{3+}. The PL emission spectra of Eu^{3+} ions are observed in $K_2CaMg(SO_4)_3$ phosphors with different concentrations under excitation of 393 nm wavelengths of light. Two well resolved prominent peaks are observed at 593nm and 613nm which are assigned to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}. Other two weak peaks are also observed at 700nm and 730nm which are assigned to $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transition of Eu^{3+}, when the sample was excited at 393nm wavelength. The strongest two peaks located at 593 nm and 613nm contribute the orange-red

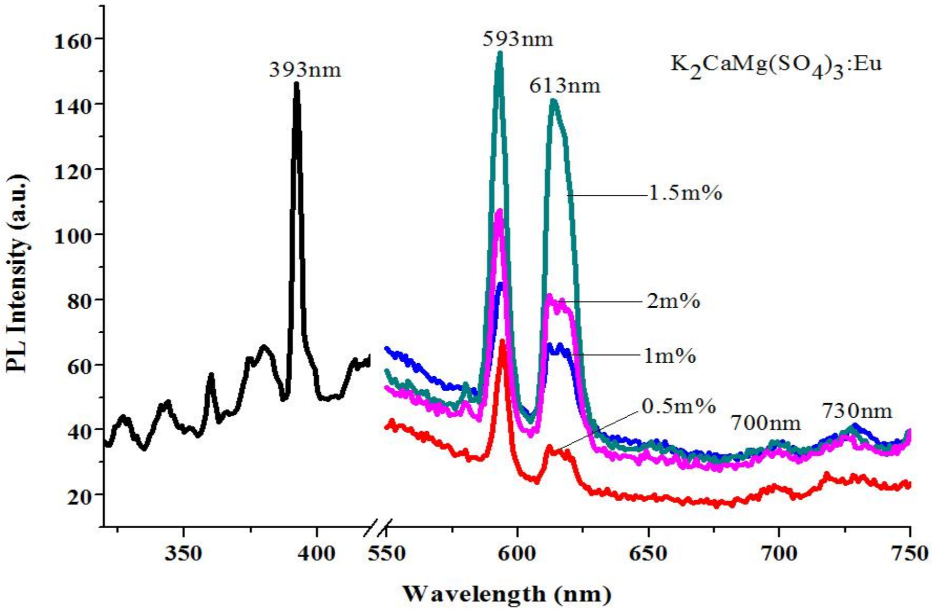

Fig. 3 PL spectra of $K_2CaMg(SO_4)_3$: x Eu^{3+} phosphor monitored at 393nm excitation.

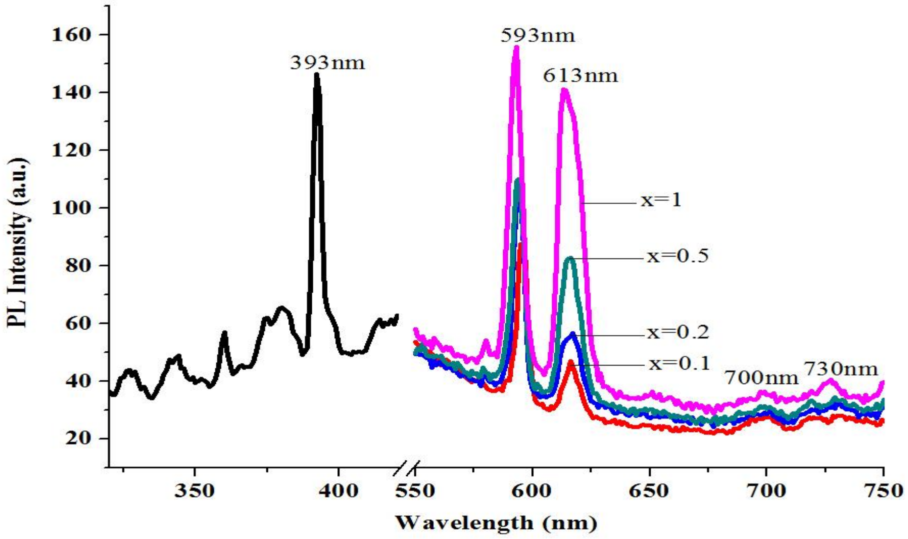

Fig. 4 PL spectra of $K_2Ca_{2-X}Mg_X(SO_4)_3$: Eu^{3+} (1.5mol %) phosphor monitored at 393nm excitation.

emission which are mainly from $^5D_0 \rightarrow {}^7F_1$ (593nm) magnetic dipole transition of Eu^{3+} ions and red emission peak at 613nm are due to $^5D_0 \rightarrow {}^7F_2$ (613nm) electric dipole transition. From Fig.3, it is clearly observed that in all the cases the intensities gradually increase up to 1.5 mol% Eu^{3+} and then decrease with increase of Eu^{3+} concentration in the $K_2CaMg(SO_4)_3$. Thus, optimum concentration for highest luminescence of Eu^{3+} concentration in our study is found to be 1.5 mol%. The quenching of luminescence with the increase of Eu^{3+} concentration which is due to the energy transfer owing between the neighboring Eu^{3+} ions. Addition of Mg in the host, affects the PL characteristics with same profile. The emission spectra of $K_2Ca_{2-X}Mg_X(SO_4)_3$: Eu^{3+} (1.5 mol %) for various content of Mg ($0.1 < x < 1$) is shown in Fig. 4. The emission intensity increases with increase in x values of Mg and the maximum at x=1. The effect of Mg content on $K_2CaMg(SO_4)_3$: Eu^{3+} is shown in Fig. 5. The figure shows that the emission intensity increases continuously and reaching a maximum at x=1 (Table 1).

Table1. Effect of Mg^{2+} ion on $K_2Ca_{2-X}Mg_X(SO_4)_3$: Eu^{3+} phosphor.

Phosphor	**λ_{ext} = 393 nm Emission Wavelength (nm)**	**PL Intensity (a.u.)**
$K_2Ca_{2-X}Mg_X(SO_4)_3$:Eu^{3+} (1.5mol%), x= 0.1	596, 616, 699, 630	87, 47, 31, 27
$K_2Ca_{2-X}Mg_X(SO_4)_3$:Eu^{3+} (1.5mol%), x= 0.2	594, 617, 700, 730	109, 54, 30, 33
$K_2Ca_{2-X}Mg_X(SO_4)_3$:Eu^{3+} (1.5mol%), x= 0.5	594, 616, 696, 729	109, 82, 34, 34
$K_2Ca_{2-X}Mg_X(SO_4)_3$:Eu^{3+} (1.5mol%), x= 1	593, 613, 700, 727	155, 141, 35, 40

According to the literature [19], the relationship between emission intensity (I) and dopant concentration (C) can be expressed as follows:

$$\log (I/C) = (-s/d) \log C + \log f \qquad \text{----------} \qquad (3)$$

where s is the index of electric multiple, variable d is the dimension of the sample, which would be equal to 3 if energy is transferred among the Eu^{3+} ions inside the particles is considered, and f is independent of the dopant concentration. The values of s are 3, 6, 8, and 10 for the exchange, electric dipole-dipole, electric dipole − quadrupole and electric quadrupole − quadrupole interactions respectively. Fig. 6 shows the log (I/C) vs log(C) plots for the $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} ions in $K_2CaMg(SO_4)_3$ phosphors. According to Eq. (3) and using linear fittings to deal with the experimental data in the region of high concentrations, the slope parameter s/d was determined to be 0.655 (close to 1), thus yielding an s value of 3. This indicates that the exchange interaction is responsible for the concentration quenching mechanism in the $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} ions in $K_2CaMg(SO_4)_3$ phosphors.

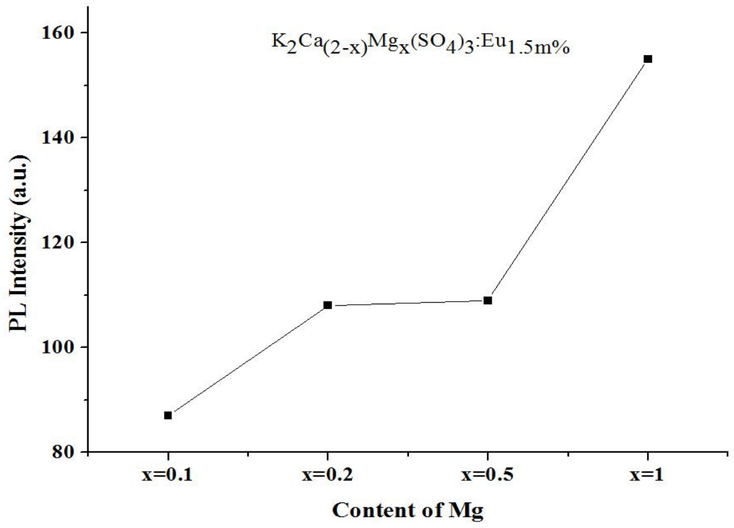

Fig. 5. Change in PL intensity with variation of Mg^{2+} content in $K_2Ca_{2-X}Mg_X(SO_4)_3$: Eu^{3+} (1.5mol %).

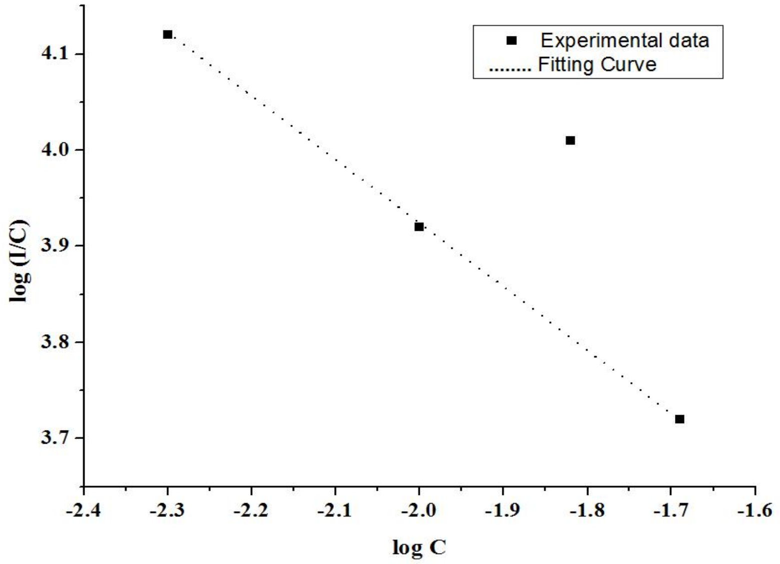

Fig. 6. The relationship between the log(C) and the log (I/C) for $K_2CaMg(SO_4)_3$: xEu^{3+} phosphor.

IV. CONCLUSIONS

$K_2CaMg(SO_4)_3$ phosphors doped with varying concentration of Eu^{3+} ions were synthesized by wet-chemical reaction method. XRD analysis confirms that the synthesized samples showed crystalline nature. PL excitation and emission spectra shows characteristic bands of Eu^{3+} ions. Concentration quenching occurs at 1.5 mol% of Eu^{3+}. Addition of Mg in the host, affects the PL characteristics with same profile. Phosphor is excited by UV wavelength and gives emission in orange-red region; hence it may be applicable as an efficient orange-red phosphor and can be used in lamp industry.

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REFERENCES

[1] A. Pandey, R.G. Sonkawde, P.D. Sahare, “Thermoluminescence and photoluminescence characteristics of nanocrystalline $K_2Ca_2(SO_4)_3$: Eu”, *J. Phys. D: Appl. Phys*, vol 35, pp 2744, 2002.

[2] S.P. Lochab, P.D. Sahare, R.S. Chauhan, Salah N., Pandey A., “Thermoluminescence and photoluminescence study of nanocrystalline $Ba_{0.97}Ca_{0.03}SO_4$: Eu”. *J. Phys. D: Appl. Phys*, vol 39, pp 1786, 2006.

[3] A. Pandey, P.D. Sahare, J.S. Bakare, S.P. Lochab, F. Singh, D. Kanjilal, “Thermoluminescence and photoluminescence characteristics of nanocrystalline $LiNaSO_4$: Eu phosphor”. *J. Phys. D: Appl. Phys*, vol 36, pp 2400, 2003.

[4] S. J. Dhoble, S. V. Moharil, T. K. Gundu Rao, “Correlated ESR, PL and TL studies on $K_3Na(SO_4)_2$: Eu thermoluminescence dosimetry phosphor”. *J. Lumin*, vol 93, pp 43, 2001.

[5] A. Deshpande, N.S. Dhoble, S.J. Dhoble, “Photo and thermoluminescence in $K_2Mg(SO_4)_2$: Dy phosphor and evaluation of trapping parameters”. *J. Lumin*, vol 180, pp 58-63, 2016.

[6] P.D. Sahare, R Ranjan., N. Salah, S.P. Lochab, “K3Na(SO4)2 : Eu nanoparticles for high dose of ionizing radiation”, *Journal of physics D: Applied Physics*, vol 40(3), pp 759, 2007.

[7] A. Pandey, V.K. Sharma, D. Mohan, R.K. Kale, P.D. Sahare, “Thermoluminescence characteristics of $K_2Ca_2(SO_4)_3$ doped with rare earths Eu and Dy”, *Journal of Physics D: Applied physics*, vol 35(12), pp 1330, 2002.

[8] N. Salah, P.D. Sahare, S. Nawan, S.P. Lochab, “Luminescence characteristics of $K_2Ca_2(SO_4)_3$:Eu, Tb micro- and nanocrystalline phosphor”, *Radiation effect and defect in solids*, vol 159 (5), pp 321-334, 2004.

[9] N. Salah, P.D. Sahare, “TL, PL and energy transfer in $K_2Ca_2(SO_4)_3$:Eu^{2+}, Ce^{3+}. *Radiation measurement*, vol 41(6), pp 665-670, 2006.

[10] N. Salah, S.P. Lochab, P.D. Sahare, *Radiation effects and defects in solids*, vol 158, pp 819-825, 2014.

[11] S.P.Puppalwar, S.J. Dhoble and Animesh Kumar, "Improvement of photoluminescence of Cu^+ ion in Li_2SO_4", *J. Bio and Chemi Luminescence* vol 26, pp 456–461, 2011.

[12] S.P.Puppalwar and S.J. Dhoble, "Development of high sensitive $LiNaSO_4$:Cu, Mg phosphor for TL dosimetry", *J. Lumin*. Vol 137, pp 245–251, 2013.

[13] S.C. Gedam, S.J. Dhoble, S.V. Moharil, "5d→4f transition in halosulphate phosphors", *J. Lumin*, vol 126(1), pp 121-129, 2007.

[14] S.C. Gedam, S.J. Dhoble, S.V. Moharil, "Eu^{2+} and Ce^{3+} emission in sulphate based phosphors", *J. Lumin*, vol 128(1), pp 1-6, 2008.

[15] G. Blasse, "On the Eu3+ Fluorescence of Mixed Metal Oxides. IV. The Photoluminescent Efficiency of Eu^{3+} Activated Oxides", *J. Chem. Phys*. Vol 45, pp 2356, 1966.

[16] G. Blasse, J. De Vries. "On the Eu3+ Fluorescence of Mixed Metal Oxides: VI . Temperature Dependence of the Fluorescence", *J. Electrochem. Soc.* Vol 114, pp 875, 1967.

[17] G. Blasse, A. Bril, W. C. Nieuport, "On the Eu^{3+} fluorescence in mixed metal oxides: Part I—The crystal structure sensitivity of the intensity ratio of electric and magnetic dipole emission", *J. Phys. Chem. Solids*. Vol 27, pp 1587, 1966.

[18] B.P. Kore, N.S. Dhoble, R.M. Kadam, S.P. Lochab, M.N Singh., S.J. Dhoble, H.C. Swart, "Thermoluminescence and EPR study of $K_2CaMg(SO_4)_3$:Dy phosphor: the dosimetric application point of view", *J. of Phy.D: Applied Physics*, vol 49, pp 9, 2016.

[19] L. Zhu, A. Lu, C. Zuo, and W Shen, "Photoluminescence and energy transfer of Ce^{3+} and Tb^{3+} doped oxyfluoride aluminosilicate glasses". *J. Alloys Compd*. Vol 509(29), pp 7789, 2011.