

Photoluminescence analysis study of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ lamp phosphors that are Eu^{2+} triggered

S.R.Choubey

*Department of Physics, vmv commerce jmt arts jip science college nagpur maharashtra india.,
Maharashtra, India**

Abstract—In the open environment, an oval series of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ triggered with Eu^{2+} phosphors was made using an easy combustion synthesis method. This process usually produces a homogenous powder. The generation of crystalline fine powder, which use reaction to release both external heat and chemical energy, is the major benefit of this technology. X-ray powder diffraction and Scanning Electron Microscopy (SEM) were used to characterize a $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphor with ultraviolet light (UV) radiation and photoluminescent emission. The $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphors were excited at 348nm and got intense blue emission at 432nm caused by the $4f^7$ to $4f^65d^1$ ion transition under UV irradiation. The discovered Blue luminescence has a lot of promise as a suitable replacement for nearly UV-excited white light that generates phosphor as a new form of phosphor when exposed to UV light.

Index Terms—Phosphor, XRD, Photoluminescence, SEM, Combustion etc.

I. INTRODUCTION

The lighting industry's current research focus is on solid-state lighting, which uses light-emitting diode (LED) and phosphor material to provide white light [1]. Solid-state lighting technology provides various advantages over traditional fluorescent lighting, including lower power consumption, compactness, efficient light production, and a longer lifetime [2]. The use of solid-state lighting will have an influence on worldwide power usage. In comparison to conventional light sources, such as incandescent light bulbs and luminescent tubes, white light-emitting diodes (LEDs) can save up to 70% of the energy and do not require any harmful ingredients [3]; thus, white LEDs have a high potential to replace them and are regarded as next

generation solid state light devices [4,5]. Because of their numerous uses in lighting and displays, phosphors based on phosphate host matrices have piqued the interest of many researchers [6-9]. The Eu^{2+} activated $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ phosphor was synthesized and its luminous characteristics were studied in this study, demonstrating that $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ is a possible phosphor for near-UV white light emitting diodes (LEDs).

II. EXPERIMENTAL

For the preparation of Eu-doped $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, europium oxide Eu_2O_3 , urea $\text{CO}(\text{NH}_2)_2$ for combustion, ammonium di-hydrogen phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ and Ammonium Fluoride NH_4F are required. For this stoichiometric composition [10-11] of the metal nitrates (oxidizers) and urea (fuel) were calculated using digital Mettler To led balance. First, Eu_2O_3 is converted into $\text{Eu}(\text{NO}_3)_3$ by mixing Eu_2O_3 into 3ml of dil. HNO_3 . Then weighed quantities of nitrate and urea were mixed together and crushed into mortar for 1hr to form a thick paste. The resulting paste is transferred to a china crucible and introduced into a vertical cylindrical muffle furnace maintained at $700 \pm 10^\circ\text{C}$. The mixture undergoes dehydration and then decomposition with the liberation of NH_3 and NO_2 . The process being highly exothermic continues and the liberated gases swell the mixture into large volume. Large exothermicity results into a flame changing the mixture into the gaseous phase. Flame temperatures as high as $1400-1600^\circ\text{C}$ convert the vapour phase oxides into mixed phosphates. The flame persists for ≈ 20 seconds. The crucible is then taken out of the furnace and the foamy product is crushed into a fine powder and got

Ca₁₀(PO)₆F₂:Eu²⁺ compound.

The concentration of Eu²⁺ has little effect on the placement of the peaks, but does enhance the intensity of the light. The symmetric emission band demonstrates that just one type of light center, Eu²⁺ ions, occupies identical locations on the grid.

Observed emission peaks of 432nm result from ⁴f₆⁵d configuration to the ⁸S_{7/2} configuration level (Fig.2). With a rise in the concentration of 0.1–1mole percent, PL intensity increases. The emission intensity has been raised maximum of 0.3 mol% of Eu²⁺ are shown in table2, which is likely owing due

to doping concentration increases.

III. RESULTS AND CONCLUSION

Photoluminescence properties

The excitation spectrum of Ca₁₀(PO₄)₆F₂:Eu²⁺ is shown in Fig.1. It encompasses many overlapping bands in the Uva re arranging from 320nm to 400nm, which are related to the ⁴f₇→⁴f₆S₁ transition of Eu²⁺. The excitation spectra are distinguished by two strong bands at 348 nm and 388 nm. This demonstrates that UV radiation may efficiently excite phosphors.

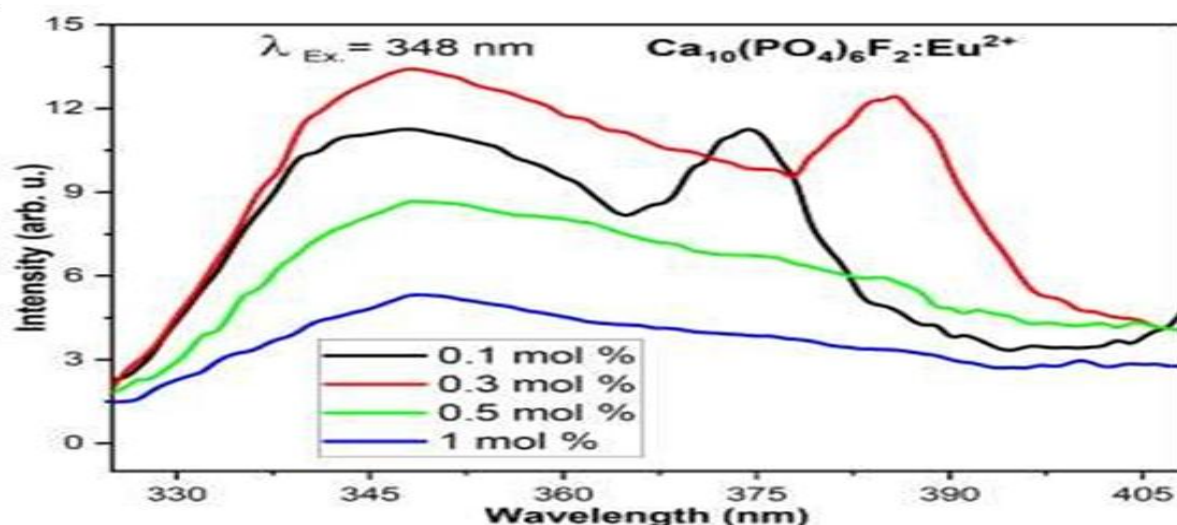


Fig.1 PL Excitation Spectrum of Ca₁₀(PO₄)₆F₂:Eu²⁺ obtained at λ_{em.}=432nm

The PL emission spectra of a Ca₁₀(PO₄)₆F₂:Eu²⁺ phosphor annealed at 700 °C is shown in Fig.2. When excited by nUV 348nm radiations attributable to the ⁴f₆⁵d₁→⁸S_{7/2} transition of Eu²⁺, the emission maximum is detected at 432 nm, with its peak intensity 11.682 are reported in table 1. The measured full width

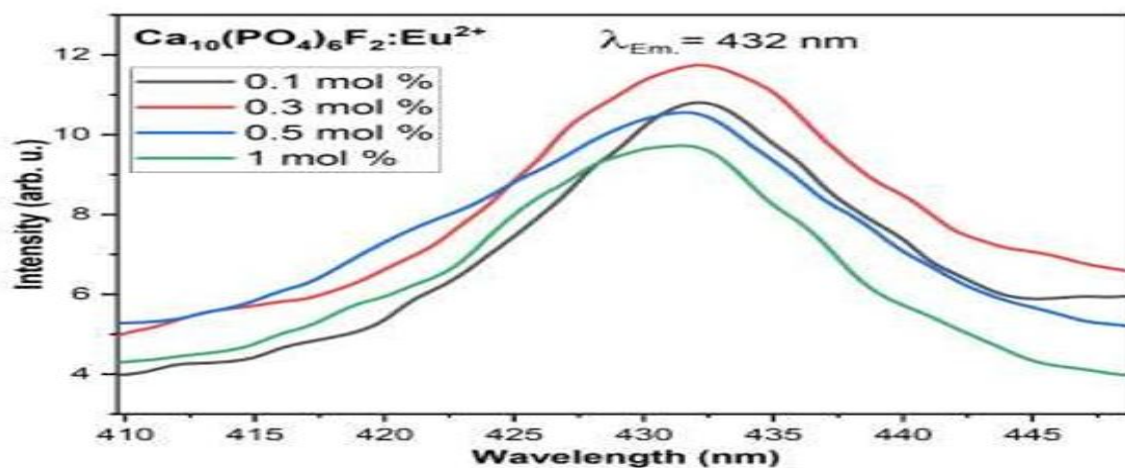


Fig.2 PL Emission Spectrum of Ca₁₀(PO₄)₆F₂:Eu²⁺ obtained at λ_{ex}= 348nm

At half maximum (FWHM) is 38 nm. There are no references against which the results may be compared. It's possible that this is the very first report. The impact of doped Eu^{2+} concentration on emission intensity was examined by synthesizing a series of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphors with $x=0, 1, 0.3, 0.5$, and 1.0 mol% phosphors with various Eu^{2+} concentrations. The relative intensity at 432 nm of Eu^{2+} ions is highly influenced by the local site symmetry around the Eu^{2+} ions. The observed rise in PL emission intensity might be attributed to a reduction in cross-relaxation between Eu^{2+} ions (in this process, an excitation transmits just a portion of its energy to another ion) with increasing Eu^{2+} concentration. The concentration quenching effect, with a further rise in Eu^{2+} concentration emission intensity has been decreased. No Eu^{3+} emission peaks in the spectrum are detected when a doping of Eu at different Eu concentrations indicates that Eu^{3+} ions may have been converted to Eu^{2+} in its matrix crystals entirely. High PL intensities in asphalt particles may be obtained without any heat treatment but for drying.

Table 1: PL emission intensities of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ (0.3 mol%) phosphor

PL Wavelength (nm)	PL Intensity (arb. unit)
432	11.682

Table 2: Concentration in mol%
V highest relative intensity of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$

Sr. No.	Concentration (mol%)	Relative Intensity (au)
1	0.1	10.73254
2	0.3	11.682
3	0.5	10.30921
4	1	9.45374

XRD studies of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ (0.1 mol%) phosphor
The crystal structure of the $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ (0.1 mol %) product was identified by X-ray powder

diffraction (XRD) using a PAN-analytical diffractometer ($\text{CuK}\alpha/1.541862 \text{ \AA}$ radiation) at a scanning speed of 100 per minute, in the 2θ range from 10° to 80° . Fig. 3 depicts the usual X-ray diffraction (XRD) patterns of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ (0.1 mol %) phosphor powder treated at 700°C . Five major peaks and many weak peaks are seen in the XRD spectra: The five major peaks are located at $2\theta=25.78, 31.02, 31.8, 32.16$, and 32.96 . These peaks relate to diffractions of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ (0.1 mol %) from the planes (112), (110), (024), and (102). Diffraction from the (103), (101), (202), and (024) planes is responsible for the comparatively weaker multipacks centered at $27.72, 29.00, 34.04, 39.88, 46.74$, and 49.46 , respectively. The strength of the peaks represented the nanoparticles high degree of crystallinity. The diffraction peaks, on the other hand, are wide, suggesting that the crystalline size is quite tiny. All of the diffraction peaks may be adequately indexed to the International Centre for Diffraction Data (ICDD)/PDF Card No. 9 Quality C, which indicate a base centered orthorhombic phase

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ (0.1 mol %) (space group $\text{P2}_1/\text{n}, 33$) with a main diffraction peak (110). $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ has an orthorhombic crystal structure (Buchwaldite), with lattice parameters of $a=0.6797$ nm, $b=0.9165$ nm, and $c=0.5406$ nm. There are no erroneous diffractions caused by crystallographic impurities discovered. The XRD pattern did not reveal the existence of elements such as $\text{Ca}(\text{NO}_3)_4\text{H}_2\text{O}$, F_2NO_3 , or $\text{NH}_4\text{H}_2\text{PO}_4$, as well as other expected phases, which is direct proof for the synthesis of the desired chemical. These findings suggest that the final product was crystalline and homogenous in nature. This demonstrates that the mixed combustion processes proceeded smoothly. There is no appreciable phase shift caused by the doped Eu^{3+} ions. Microspheres have a greater crystallinity than irregular particles.

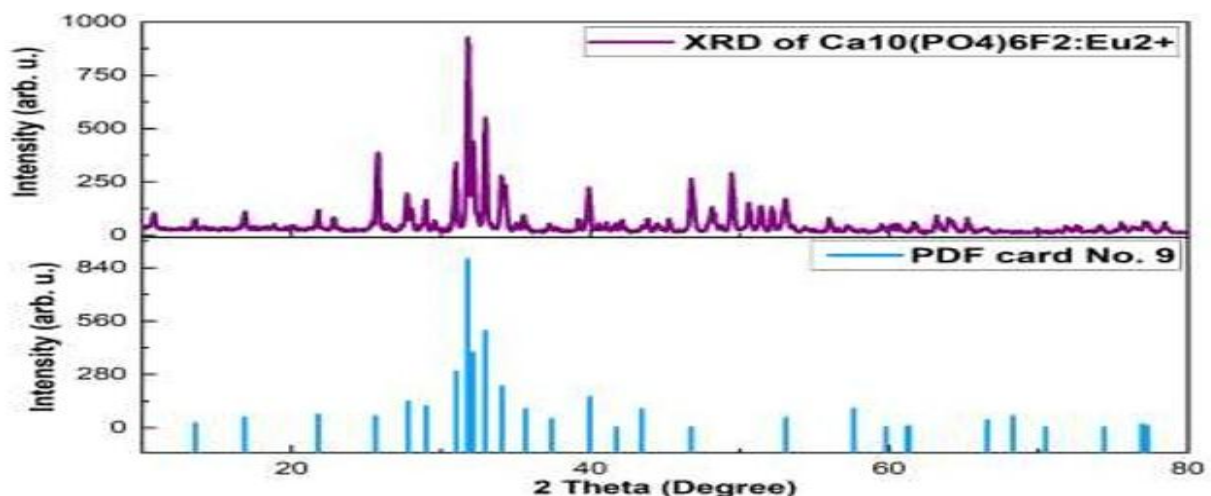


Fig.3 X-Ray Diffraction Pattern of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}(0.1\text{mol}\%)$

The Debye-Scherrer formula [12-15] was used to get the average particle size. $D = 0.9\lambda / \beta \cos\theta$, where λ is the X-ray wavelength ($\lambda = 1.541862 \text{ \AA}$), β is the diffraction line broadening measured at half of its highest intensity (FWHM: Full Width at Half Maximum), θ is the Bragg's diffraction and D is the particle diameter size. $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphor has an average crystallite size of 38.85 nm. This demonstrates that nano crystalline phosphor may be formed using the combustion synthesis approach. Scanning Electron Microscopy Analysis of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}(0.5\text{mol}\%)$

To identify the morphology of nanoparticles, the

sample was subjected to SEM studies [16]. Fig. 4 (a) and (b) are typical SEM photos illustrating the shape of the produced nano particles of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}(0.5\text{mol}\%)$ phosphor with the magnification of 2.54 and 7.79kx respectively. The SEM shows cylindrical structures with petals having petal length of $4\mu\text{m}$ with a basal width of $1.0\mu\text{m}$. SEM pictures show that homogenous materials were obtained as micro metric aggregates of nanosized features. These micro aggregates are made up of cylindrical particles with a diameter of $4.0\mu\text{m}$.

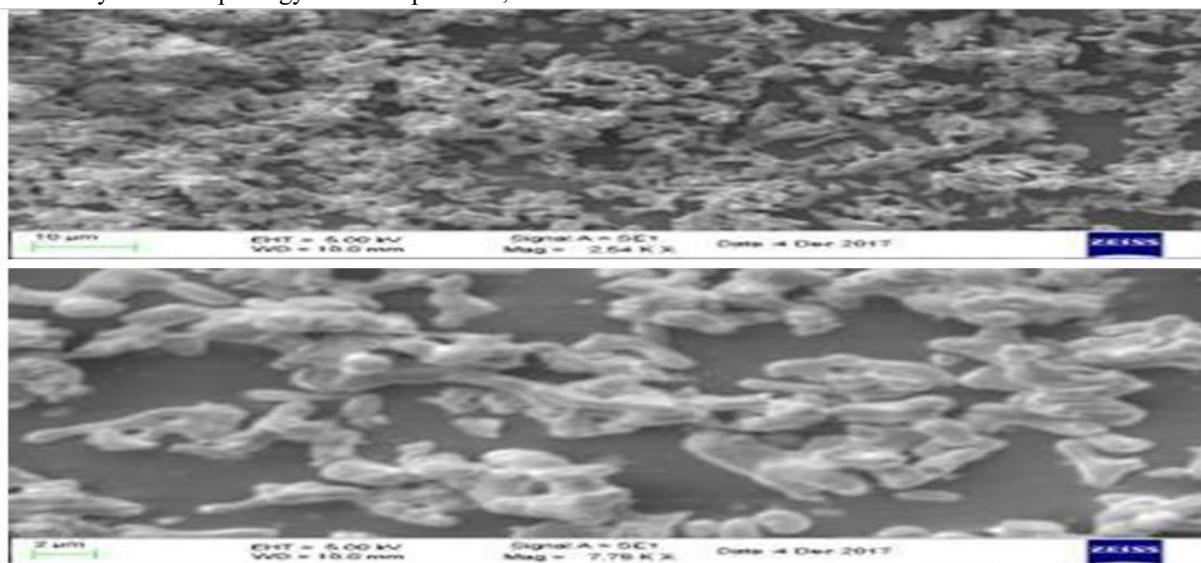


Fig.4 SEM images of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphor

(a) 0.5mol %, $10\mu\text{m}$, with mag=2.54kx

(b) 0.5mol %, $2\mu\text{m}$, with mag=7.79kx

The estimated grain sizes of the samples from the SEM image are bigger than those obtained from the XRD study. The presence of certain bigger nano particles might be ascribed to the nano particles tendency to agglomerate as a result of their high surface energy.

Fourier Transform Infrared Spectroscopy Graph of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$

For structural elucidation and chemical identification, FT-IR spectroscopy is a significant and powerful technique [17]. Fig. 5 shows the FTIR transmittance spectrum of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ for the $4000\text{--}500\text{cm}^{-1}$ spectral range. The literature indicates that this spectrum is characteristic of orthophosphates.

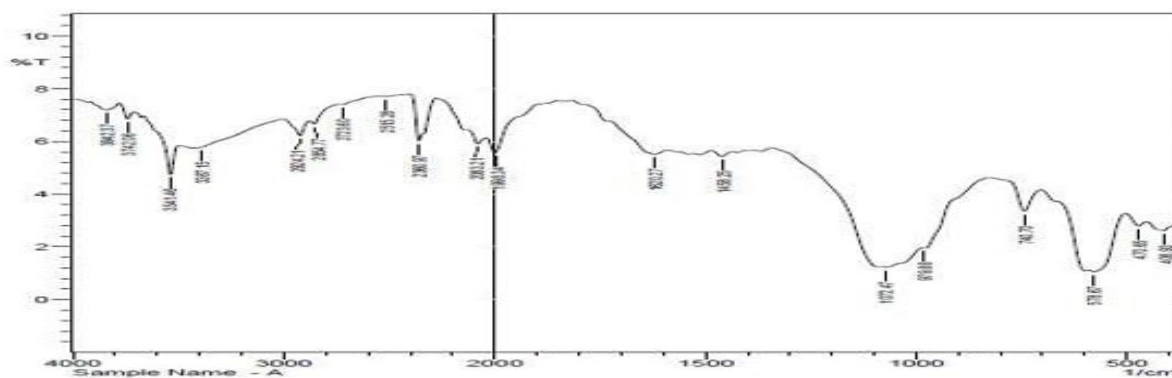


Fig.5 FTIR Transmittance Graph of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphor

The antisymmetric stretching modes of the exterior PO_3 groups are allocated the most intense complex band at 578.67cm^{-1} . The band at 408.93cm^{-1} corresponds to the symmetric P–O–P bridge frequency, which may have a minor to and fro shifting and is widely regarded as the most distinctive for orthophosphates. In the pyrophosphate spectra, there are no bands in this frequency range. When the P–O–P link is not linear, the band at 750cm^{-1} is stronger in Raman spectra of pyrophosphates but weaker in IR spectra. At 1072cm^{-1} , the $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ spectrum exhibits antisymmetric

P–O–P modes.

CIE Co-ordinates of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphor

$x = 0.333$ and $y = 0.333$ are the optimal white light chromaticity coordinates. In general, the closer the CIE chromaticity coordinates are to these locations, the greater the quality of white-in the blue light area.

Table 3 shows the CIE chromaticity coordinates values computed from $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphor emission spectra. It can be seen that when doping concentration increases, the CIE chromaticity coordinates values drop.

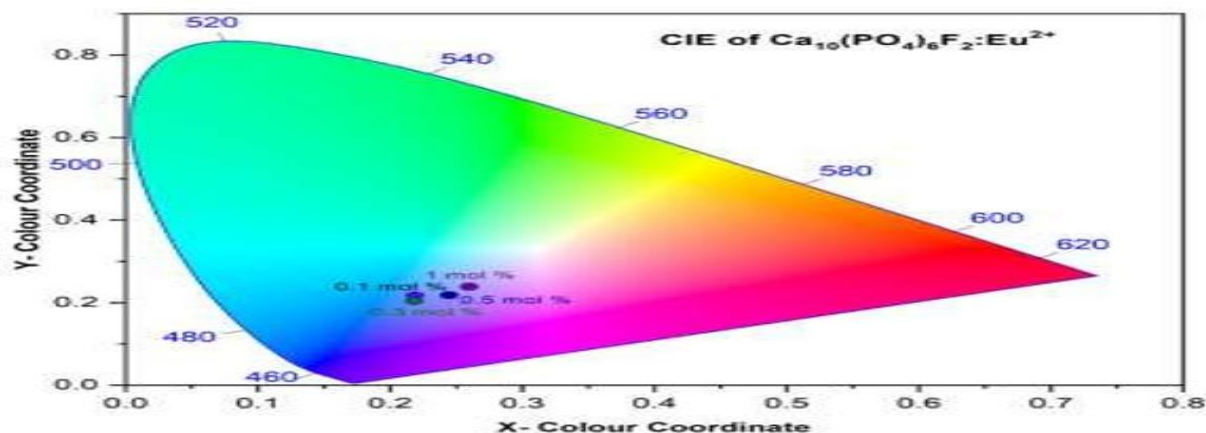


Fig.6 CIE chromaticity graph of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ system

The color co-ordinates for the greatest emission intensity $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ (0.3 mol percent) sample are $x=0.2181$ and $y=0.2044$. It implies that the color characteristics of the $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphor generated through combustion synthesis

approach those necessary for field emission displays. $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphor was found as a potential and fascinating material capable of emitting strong blue luminescence.

Table3:CIE chromaticity coordinates values $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ system

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$	mol %	0.1	0.3	0.5	1	Colour
CIE Chromaticity Coordinates Values	x	0.2185	0.2181	0.2445	0.2597	Blue
	y	0.2176	0.2044	0.2183	0.2389	

IV. CONCLUSION

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ doped with the rare earth ion Eu^{2+} was reported in this study and validated by XRD. Characterization of photoluminescence of produced phosphors revealed the significance of rare earth ions in the host lattice. Excitation and emission spectra were used to characterize the produced phosphors PL spectroscopy. When excited at 348 nm, the emission spectra of Eu^{2+} Activated $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ phosphor reveals a strong peak at 432 nm (blue). The blue area of the spectrum was utilized to have LED emission. This work demonstrated that the $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphors may be used in LEDs. This work described the production of effective phosphate-based phosphors using a combustion process, which was characterized by an X-ray diffraction (XRD) pattern, morphological analysis with a scanning electron microscope (SEM), and photoluminescence behavior of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ doped with Eu^{2+} . According to the findings, this phosphor has potential uses in the field of LED-based illumination.

REFERENCES

- [1] P.L.Li, L.B.Pang, Z.J.Wang, Z.P.Yang, Q.L.Guo, X.Li, J. Alloys Compd. 478 (2009) 813.
- [2] Höpfe H.A. Recent developments in the field of inorganic phosphors. Angew. Chem. Int. Ed., 2009, 48 (20): 3572.
- [3] Chan Tingshan, Liu Rushi, Ivan Baginskiy. Synthesis, crystal structure, and luminescence property of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphor for field emission displays. Chem. Mater., 2008, 20: 1215.
- [4] M.M.Haque, H.I.Lee, D.K.Kim, J. Alloy Compd. 481 (2009) 792.
- [5] X.H.He, M.Y.Guan, N.Lian, J.H.Sun, T.M.Shang, J. Alloys Compd. 492 (2010) 452.
- [6] Y.H.Song, G.Jia, M.Yang, Y.J.Huang, H.P.You, H.J.Zhang, Appl. Phys. Lett. 94 (2009) 091902.
- [7] Helmut Ehrenberg, Sonja Laubach, P.C.Schmidt, R.McSweeney, M.Knapp, K.C.Mishra, Journal of Solid State Chemistry 179 (2006) 968.
- [8] K.Murakami, J.Narito, Y.Anzai, H.Itoh, S.Doi, K.Awazu, J. Illum. Eng. Jpn. 3 (1979) 6.
- [9] Chuanxiang Qin, Yanlin Huang, Wanxue Zhao, Liang Shi, Hyo Jin Seo, Materials Chemistry and Physics 121 (2010) 286.
- [10] S. A. Pardhi, V. R. Panse and S. J. Dhoble, Journal of biological and chemical luminescence, 1290-1294, 31. 2016
- [11] V.R. Panse, N.S. Kokode, S.J. Dhoble, J. Chem. Biol. Phys. Sci. 4 (2014) 3736–3744.
- [12] N.S. Kokode, V.R. Panse, S.J. dhoble, J. Adv. Mater. Lett. 6 (7) (2015) 616–619
- [13] K.-S. Sohn, S.H. Cho, S.S. Park, N. Shin, Appl. Phys. Lett. 89 (2006) 051106.
- [14] Kenji Toda, Journal Alloys and Compounds 665, 408 (2006)
- [15] K.N. Shinde and K. Park, Luminescence 2013; 28: 793–79
- [16] Hee-Suk Roh, Seyoon Hur, Hee Jo Song, Ik Jae Park, Do

ngKyunYim,DongWanKim,KugSunHong,
MatLett70 (2012) 37.

- [17] Z.C.Wu,J.X.Shi,J.
Wang,M.L.Gong,Q.Su,JSolidStateChem179(2
006)2356.
- [18] V.R.Panse,ResultsinPhysics7(2017)178-182