



PHOTOLUMINESCENCE AND CHARACTERIZATION OF EU²⁺ DOPED CA₁₀(PO₄)₆F₂ PHOSPHOR

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Communicated : 15.01.2023

Revision : 20.02.2023 & 02.03.2023
Accepted : 27.03.2023

Published : 30.05.2023

ABSTRACT:

In the open environment, a novel series of Ca₁₀(PO₄)₆F₂ triggered with Eu²⁺ phosphors was made using an easy combustion synthesis method. This process usually produces a homogenous powder. The generation of crystalline fine powder, which uses 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 characterise a Ca₁₀(PO₄)₆F₂:Eu²⁺ phosphor with ultraviolet light (UV) radiation and photoluminescent emission. The Ca₁₀(PO₄)₆F₂:Eu²⁺ phosphors were excited at 348 nm and got intense blue emission at 432 nm caused by the ⁴f₇ to ⁴f₆ ⁵d₁ 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.

Keywords :- Phosphor, XRD, Photoluminescence, SEM, Combustion etc.

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 Eu²⁺ activated Ca₁₀(PO₄)₆F₂ phosphor was synthesised and its

luminous characteristics were studied in this study, demonstrating that Ca₁₀(PO₄)₆F₂ is a possible phosphor for near-UV white light emitting diodes (LEDs).

EXPERIMENTAL:

For preparation of Eu doped Ca₁₀(PO₄)₆F₂, Calcium nitrate Ca(NO₃)₂.4H₂O, Europium oxide Eu₂O₃, urea CO(NH₂)₂ for combustion, ammonium di-hydrogen phosphate NH₄H₂PO₄ and Ammonium Fluoride NH₄F are required. For this stoichiometric composition [10-11] of the metal nitrates (oxidizers) and urea (fuel) were calculated using digital Mettler Toledo balance. First of all, Eu₂O₃ is converted into Eu(NO₃)₃ by mixing Eu₂O₃ into 3 ml of dil. HNO₃. 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±10°C. The mixture undergoes dehydration and then decomposition with liberation of NH₃ and NO₂. 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 gaseous phase. Flame temperature as high as 1400-1600°C converts 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 $\text{Ca}_{10}(\text{PO})_6\text{F}_2:\text{Eu}^{2+}$ compound.

RESULTS AND CONCLUSION:

Photoluminescence properties

The excitation spectrum of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ is shown in Fig.1. It encompasses many overlapping bands in the UV area ranging from 320 nm to 400 nm, which are related to the $4f_7 \rightarrow 4f_65s_1$ transition of Eu^{2+} . The excitation spectra is distinguished by two strong bands at 348 nm and 388 nm. This demonstrates that nUV radiations may efficiently excite phosphor.

The PL emission spectra of a $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphor annealed at 700 °C is shown in Fig.2. When excited by nUV 348 nm radiations attributable to the $4f_65d_1 \rightarrow 8s_{7/2}$ transition of Eu^{2+} , the emission maximum is detected at 432 nm, with its peak intensity 11.682 au reported in table 1. The measured full width 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 synthesising a series of $\text{Ca}_{10(1-x)}(\text{PO}_4)_6\text{F}_2:\text{Eu}_x^{2+}$ powders 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 excited ion transmits just a

portion of its energy to another ion) with increasing Eu^{2+} concentration.

The concentration of Eu^{2+} 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 centre, Eu^{2+} ions, occupies the identical locations on the grid. Observed emission peaks of 432 nm result from $4f_65d$ configuration to the $8s_{7/2}$ configuration level (Fig.2). With a rise in the concentration of 0.1–1 mole percent, PL intensity increases. The emission intensity has been raised maximum for 0.3 mol% of Eu^{2+} are shown in table 2, which is likely owing due to 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 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.

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 (CuK α /1.541862 Å⁰ 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 $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}_{0.1}$ 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 percent) from the planes (112), (110), (024), and (102). Diffraction from the (103), (101), (202), and (024) planes is responsible for the comparatively weaker multiplexes centred 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 indicated a base centered orthorhombic phase $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ (0.1 mol %) (space group $P21/n,33$) 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.

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 nanocrystalline 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 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 nanoparticles of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ (0.5 mol %) phosphor with the magnification of 2.54 and 7.79 kx respectively. The SEM shows cylindrical structures with petals having petal length of 4 μm with a basal width of 1.0 μm .

SEM pictures show that homogenous materials were obtained as micrometric aggregates of nanosized features. These micro aggregates are made up of cylindrical particles with a diameter of 4.0 μm . 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 nanoparticles might be ascribed to the nanoparticles 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 4000-500 cm^{-1} spectral range. The literature indicates that this spectrum is characteristic of orthophosphates. The antisymmetric stretching modes of the exterior PO_3 groups are allocated the most intense complex band at 578.67 cm^{-1} . The band at 408.93 cm^{-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 750 cm^{-1} is stronger in Raman spectra of pyrophosphates but weaker in IR spectra. At 1072 cm^{-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-light emission [18]. The chromaticity coordinates of emission bands may be changed by varying the fraction of dopant (Eu^{2+}) accessing two types of lattice sites in the $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ host (Ca). In Fig. 6 sphere symbols represent the changes in CIE chromaticity coordinates for the produced samples. In the CIE-1931 chromaticity diagram, practically all of the prepared samples' chromaticity coordinates are 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. The colour 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 colour 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.

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 characterise the produced phosphors PL spectroscopy. When excited at 348 nm, the emission spectra of Eu-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 utilised 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 characterised by an X-ray diffraction (XRD) pattern, morphological analysis with a scanning electron microscope (SEM), and photoluminescence behaviour 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.

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Table 1: PL emission intensities of Ca₁₀(PO₄)₆F₂:Eu²⁺ (0.3mol %) phosphor

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

Table 2: Concentration in mol % Vs highest relative intensity of Ca₁₀(PO₄)₆F₂:Eu²⁺

| 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 |

Table 3 : CIE chromaticity coordinates values Ca₁₀(PO₄)₆F₂:Eu²⁺ system

| Ca ₁₀ (PO ₄) ₆ F ₂ :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 | |

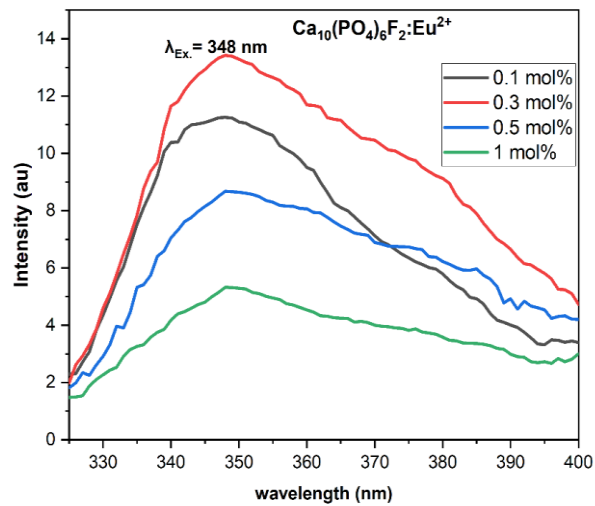


Fig. 1 PL Excitation Spectrum of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ obtained at $\lambda_{\text{em}} = 432 \text{ nm}$

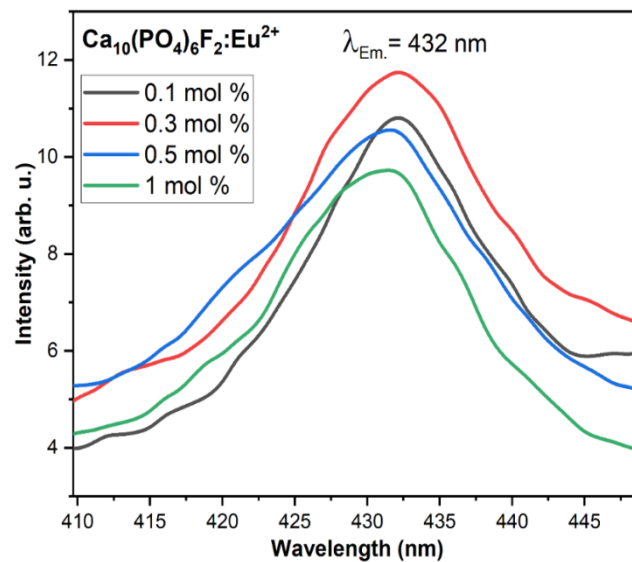


Fig. 2 PL Emission Spectrum of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ obtained at $\lambda_{\text{ex}} = 348 \text{ nm}$

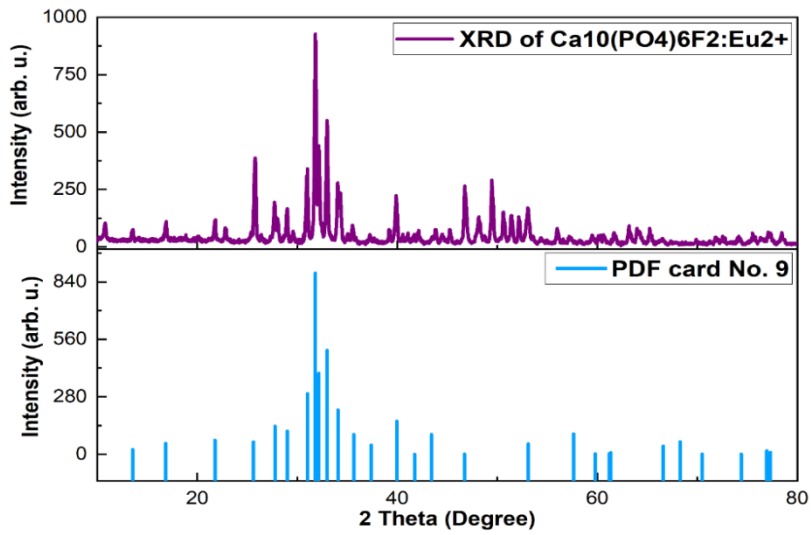


Fig. 3 X-Ray Diffraction Pattern of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ (0.1 mol %)

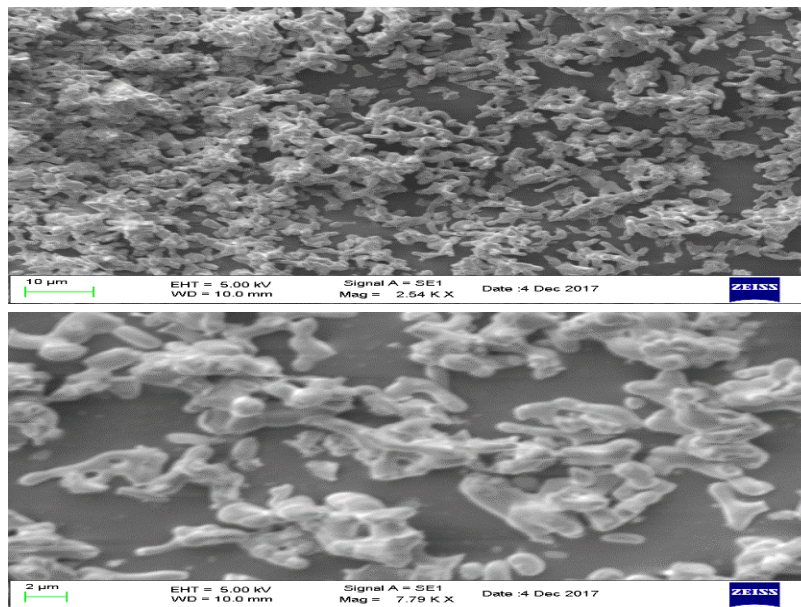


Fig. 4 SEM images of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ phosphor (a) 0.5 mol %, 10 µm, with mag=2.54 kx (b) 0.5 mol %, 2 µm, with mag=7.79 kx

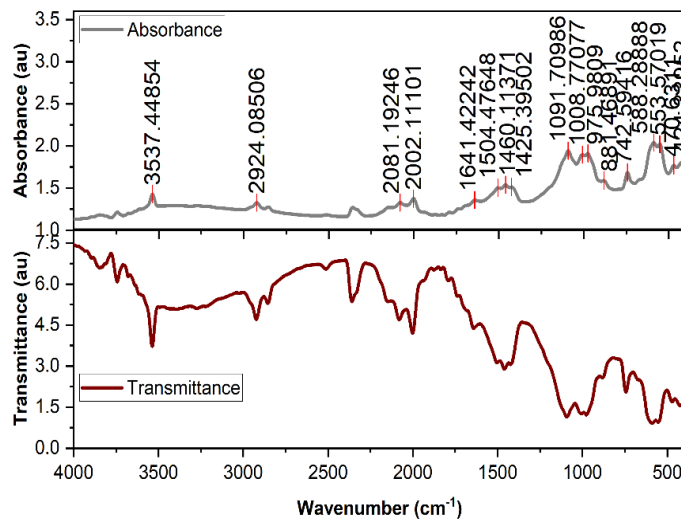


Fig. 5 FTIR Transmittance Graph of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ 400-4000 cm^{-1}

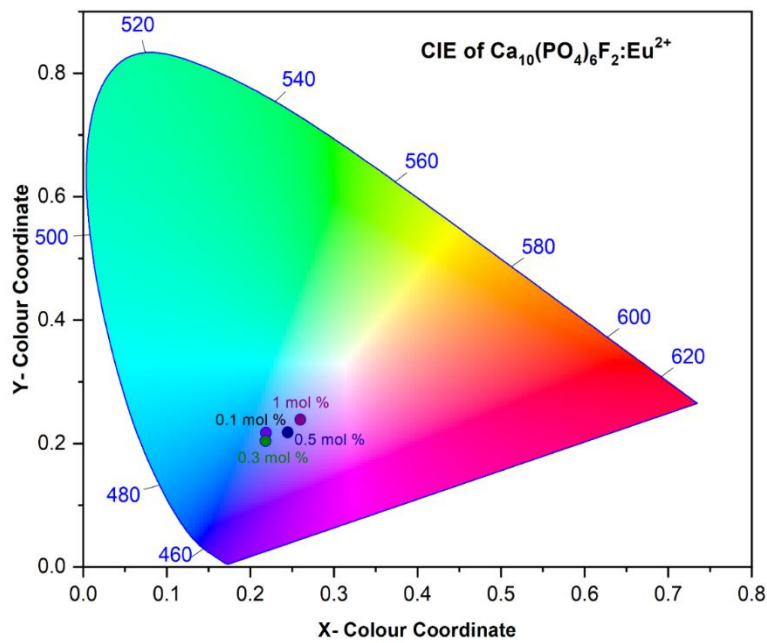


Fig. 6 CIE chromaticity graph of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ system