

Influence of sol-gel, combustion, and solid-state synthesis methods on the structural and photoluminescence properties of $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{xEu}^{3+}$ phosphor materials for LEDs applications.

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Abstract. $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{xEu}^{3+}$ ($x = 0, 1\%$) phosphor materials were successfully synthesized using three synthesis methods namely, sol-gel, combustion, and solid-state, to investigate the influence of each synthesis method on the structural and photoluminescence properties of the prepared materials. A cubic crystal structure was confirmed in all synthesis methods via the X-ray diffraction (XRD) technique. Scanning electron microscopy (SEM) revealed smooth-like morphologies with sharp edges for the sol-gel and heterogeneous morphology for the combustion method, which included hexagonal-like structures. Moreover, largely agglomerated cubic-like particles were observed in the solid-state method. The average particle size distribution ranged from 500 to 890 nm for all methods. To evaluate photoluminescence emission properties, the samples were excited at two wavelengths, 246 and 395 nm. Intense photoluminescence emission was observed at approximately 615 nm for both excitation wavelengths across all synthesis methods; however, there were some variations in emission intensity across the synthesis methods. An intense emission peak at 615 nm is ascribed to $^5\text{D}_0 \rightarrow ^7\text{F}_j$ electric dipole transitions of Eu^{3+} , implying efficient energy transfer between $\text{Zn}_4\text{B}_6\text{O}_{13}$ and Eu^{3+} . The sol-gel method produced intense emission compared to other methods, which suggests that it is the most optimized method. The sol-gel method exhibited the highest PL intensity, followed by the solid-state method, and finally the combustion method. The chromaticity diagram revealed that all prepared phosphor materials exhibited red-color emissions. Red-coloured emissions indicate successful incorporation of Eu^{3+} ions into the host lattice. The synthesized phosphor materials are regarded as potential candidates for red LEDs in solid-state lighting systems.

1 Introduction

Research focusing on cost effective, energy-saving, longlife span, and environmentally friendly luminescent materials is still ongoing. Luminescent materials are very significant in the manufacturing of solid-state lamps and light-emitting diodes (LEDs). Solid-state lighting is regarded as energy-efficient, environmentally friendly, long lifetime and it has low power consumption [1]. The quality of the prepared phosphor material is influenced by the type of synthesis method. Incorporation of rare earth ions in the host material enhances its luminescence efficiency as it introduces new impurities in its band gap, either by single ion incorporation or co-doping [2]. There are two methods used to produce commercial white light-emitting diodes (wLEDs): Firstly, the blue LED chip Gallium Nitride (GaN) is incorporated into yellow Yttrium aluminium garnet doped with cerium (YAG: Ce^{3+}), and the second method involves the mixing of tri-phosphor materials (red-green-blue: RGB) excited by the ultraviolet light. These commercial wLEDs have a low colour rendering index ($\text{CRI} < 70$) and a higher correlated colour temperature ($\text{CCT} > 327^\circ\text{C}$) due to the lack of a red phosphor [3], [4]. To overcome this drawback, Eu^{3+} is introduced as a doping agent.

The following inter-configurational transitions $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$) are responsible for the well-known red emission when Eu^{3+} ions are introduced in various host materials. There are numerous advantages of using Eu^{3+} ion as doping agent such as reducing the bandgap of the material and improving its conductivity, and repositioning the valence and the conduction band of the host material [5], [6]. Numerous researchers have reported on the Zinc borate-based phosphor materials. For instance, Liang Pan et al. [4] reported on the synthesis of $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu/Tb}$ materials using the conventional solid-state method to study their spectroscopic behaviour. Meijerink et al. [7] reported on the synthesis of $\text{Zn}_4\text{B}_6\text{O}_{13}$ using the solid-state method for their photoluminescence and thermoluminescence properties. Zhao et al. [8] reported on the synthesis of $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Tb}^{3+}, \text{Yb}^{3+}$ using the solid-state reaction method to study its multimodal emission for information encryption and anti-counterfeiting.

2 Experimental

2.1 Sample preparation

Different chemical synthesizing techniques, such as sol-gel, combustion, and solid-state reaction routes, offer the unique possibility of generating high-purity nanophosphors with different morphologies. For preparation, zinc nitrate ($\text{Zn}(\text{NO}_3)_2(6\text{H}_2\text{O})$ (99%) was used as an oxidizer. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) (99.95%) and boric acid (H_3BO_3) (99.5%) are added as fuels. For the sol-gel method, ($\text{Zn}(\text{NO}_3)_2(6\text{H}_2\text{O})$ (99%) and (H_3BO_3) (99.5%) were dissolved in 40 ml of hot deionized ($\text{DI-H}_2\text{O}$) water, whereas, ($\text{C}_6\text{H}_8\text{O}_7$) (99.95%) was liquified in a separate beaker with 40 ml of $\text{DI-H}_2\text{O}$ and later added to a mixture of zinc nitrate and boric acid while stirring it, to promote homogeneity in the mixture of reactants. Europium (III) nitrate hexahydrate $\text{Eu}(\text{NO}_3)_3(6\text{H}_2\text{O})$ (99.99%) is used as Eu^{3+} source. Consequently, a gel-like solution was formed and was allowed to strengthen by letting it age overnight and heated at 200 °C. In the combustion method, ($\text{Zn}(\text{NO}_3)_2(6\text{H}_2\text{O})$ (99%) and (H_3BO_3) (99.5%) were liquified in one beaker of 40 ml of hot $\text{DI-H}_2\text{O}$ water, while urea was dissolved in a separate beaker with $\text{DI-H}_2\text{O}$. After urea was completely dissolved in deionized water, it was then added to a mixture of zinc nitrate and boric acid while being continually stirred, and this allowed for the formation of a homogeneous mixture. A few drops of approximately 10 ml of NH_4OH were added to the prepared solution prior to reaching pH 9 after approximately 30 minutes. Subsequently, a precipitate was formed and then placed in a furnace. Afterwards, the sample was taken out of the furnace and ground using a pestle and mortar. In the solid-state reaction method, precursors were mixed in proper stoichiometric proportions and ground for approximately 20 minutes using an agate pestle and mortar. The mixture was then homogenized using acetone. All the resulting samples were heated in a furnace at 800 °C for 2 hours and subsequently annealed at 900 °C. The final prepared samples were then made available for characterization using various techniques.

2.2 Characterization techniques

The $\text{Zn}_4\text{B}_6\text{O}_{13}$ and $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ nanophosphors were characterized by X-ray diffraction to determine their crystal structure using an XRD D8 Advanced (AXS GmbH) diffractometer. The morphology and elemental composition of the prepared materials were analysed using FE-SEM coupled with EDS system (JEOL JSM-7800F). Photoluminescence properties were studied using the Varian Carry Eclipse and the FLS 980 spectrophotometers.

3 Results and Discussion

3.1 XRD patterns of the $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ phosphors

Figure 1 (a-d) shows the X-ray diffraction (XRD) patterns for the $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ (where x is 1 mol%) phosphor synthesized with the (a) combustion, (b) solgel, and (c) solid-state methods, respectively, where fig. 1(d) is the standard background XRD patterns of the $\text{Zn}_4\text{B}_6\text{O}_{13}$ structure (JCPDS No: 01-076-0917), with a space group of I-43. The diffraction peaks were found around 2θ angles of 24°, 29°, 38°, 45°, 49°, 52°, 58°, 61°, 63°, 69°, 71°, 74°, 76°, and 79°, corresponding to miller indices of (200), (211), (310), (321), (400), (330), (420), (422), (510), (521), (440), (433), (600), and (532), respectively. The calculated lattice parameters for the sample synthesized using the combustion method are as follows $a = b = c = 7.47407 \text{ \AA}$, with a cell volume of $417.51 \text{ \AA}^3$. The calculated lattice parameters for the sample synthesized using the sol-gel are as follows: $a = b = c = 7.47547 \text{ \AA}$, with a cell volume of $417.75 \text{ \AA}^3$. The calculated lattice parameters for the sample synthesized using the solid-state reaction method are as: $a = b = c = 7.47148 \text{ \AA}$, with a lattice volume of $417.51 \text{ \AA}^3$. Lastly, the calculated lattice angles in all synthesis methods are $\alpha = \beta = \gamma = 90^\circ$, confirming the cubic crystal structure [8].

The Debye-Scherrer equation was used to calculate the average crystallite particle sizes of the synthesized nanophosphors [9].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where D is the average crystallite size, k is the shape correction factor of taken as 0.9, θ is the diffraction angle, and β is the full width at half maximum (FWHM) for the diffraction peak. The wavelength of the X-ray source (0.15406 nm) is denoted by λ . The most intense peak indexed as (211) acts as a fingerprint peak for crystallite estimation of all the $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ phosphors, which is observed from the XRD spectra (Fig 1) in all synthesis methods used in this study. The sharpness and high intensity of the (211) peak suggest high crystallinity [10]. The average crystallite sizes produced for $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ phosphor materials were found as 98.05nm, 96.81 nm, and 95.93 nm for sol-gel, solid-state, and combustion methods, respectively. Small crystallite sizes within the nanometer range with well-defined crystal structures tend to suppress non radiative recombination pathways, allowing radiative recombination pathways, and enhances photoluminescence efficiency of a material [11].

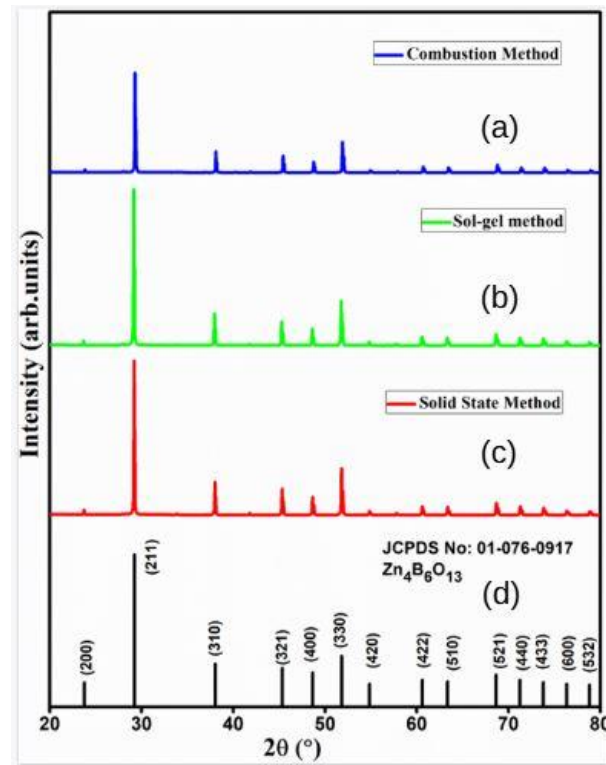


Figure 1. XRD patterns of $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{xEu}^{3+}$ (where $x = 1\%$) nanophosphors prepared through: (a) Sol-Gel, (b) Combustion, and (c) Solid-state reaction method, and (d) JCPDS standard peaks for the host $\text{Zn}_4\text{B}_6\text{O}_{13}$.

Table 1. Crystallite size of $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{xEu}^{3+}$ (where $x = 1\%$) nanophosphors prepared through: (1) Sol-Gel, (2) Combustion, and (3) Solid-state reaction method.

Sample No	Sample	Crystallite size (nm)
1	$\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ (Sol-gel)	98.05
2	$\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ (Combustion)	95.93
3	$\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ (Solid-state)	96.81

3.2 Morphological studies

The morphology of the prepared samples was examined through scanning electron microscopy (SEM). Figure 2 depicts the SEM micrographs for the $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ synthesized by the (a) sol-gel, (b) combustion, and (c) solid-state methods. The micrographs show agglomerated particles for all synthesis methods. Figure 2 (a) shows a combination of smooth cubic and other polyhedron-like morphologies without any apparent pores as shown in the blue circle. The large spaces indicated by the blue arrows are from the specimen holder (bare glass slide). Figure 2 (b) depicts particles with heterogeneous morphologies, rough like with sharp edges. Particles are agglomerated, arranged in scattered, distinct clusters. Large particles are surrounded by smaller particles and separated by large areas of uncovered substrate, as indicated by arrows pointing to the bare substrate areas. The $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ phosphors depicted in Fig 2 (c) conveyed hexagonal and cubic morphological structures. In addition, these particles are largely agglomerated into distinct groups and are randomly distributed on the specimen holder, as depicted by the red circles. The large gaps denoted by the red arrows are due to the specimen holder and not the sample. Fig 2(d), (f) and (e) showed the measured average particle sizes of the $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ phosphor. They were found to be 890 nm, 750 nm, and 500 nm for sol-gel, solid-state, and combustion methods, respectively.

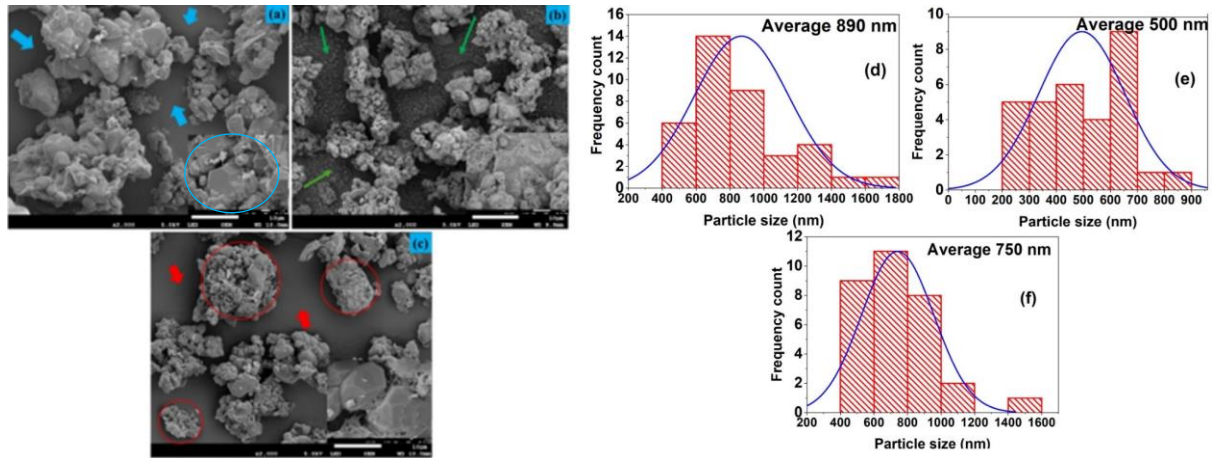


Figure 2. Field-emission scanning electron microscopy (FE-SEM) images of $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{x}\text{Eu}^{3+}$ (where $\text{x} = 1\%$) nanophosphors prepared by: (a) Sol-gel (b), Combustion, (c) Solid-state reaction methods and the histograms displaying the average particle size distribution of $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ nanophosphors prepared by (d) sol-gel, (e) combustion, and (f) solid-state methods.

3.3 Photoluminescence studies of $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Eu}^{3+}$ phosphors using different techniques

Figure 3 (a) and (b) display the PL excitation and emission spectra respectively. The emission spectra were obtained by exciting the samples by the prominent wavelength of around 246 nm in the excitation spectra. It is clear that the prominent wavelength in the emission spectra is centred around 614 nm. The excitation used is at the prominent wavelength of 246 nm as obtained in the excitation spectrum in Fig 3 (a). The excitation spectra for combustion and solid-state methods show the excitation peaks at 320, 360, 385, 396, 470, 525, and 530 nm, which are attributed to the ${}^7\text{F}_0 \rightarrow {}^5\text{H}_3$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{G}_1$, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$, and ${}^7\text{F}_1 \rightarrow {}^5\text{D}_1$ inter-configurational transitions of Eu^{3+} ions, respectively. Where ${}^7\text{F}_0 \rightarrow {}^5\text{G}_1$ is the weaker magnetic dipole transition from the ground state manifold of ${}^7\text{F}_0$ to the higher lying ${}^5\text{G}_1$ manifold, with $j=1,2,3,4$ depending on the energy level. The wide bands within the 250 nm region are associated with the charge transfer band between the 2p orbital of O^{2-} and the 4f orbital of Eu^{3+} [4]. The excitation peaks with the highest intensity correspond to 246 nm [12].

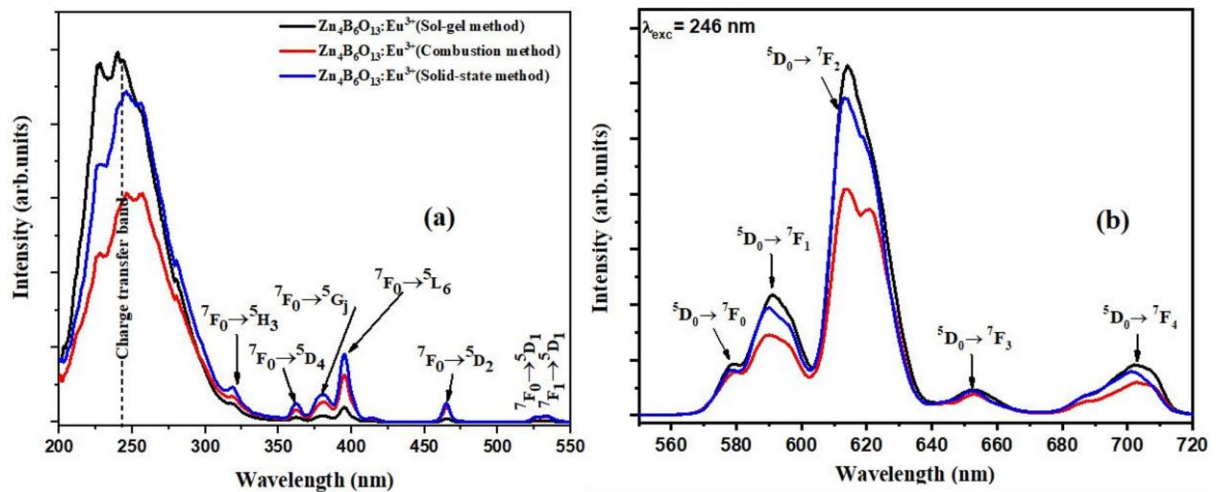


Figure 3. (a) Photoluminescence excitation and (b) emission spectra of $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{x}\text{Eu}^{3+}$ (where $\text{x} = 1\%$) nanophosphors prepared by: (1) Sol-gel, (2) Combustion, (3) Solid-state reaction methods using the parameters of $\lambda_{\text{emi}} = 614 \text{ nm}$ and $\lambda_{\text{exc}} = 246 \text{ nm}$ wavelengths.

Figure 3 (b) shows the emission spectrum of the prepared samples at an excitation wavelength of 246 nm. There are $^5D_0 \rightarrow ^7F_j$ (where $j=1, 2, 3$, and 4) transitions of $Zn_4B_6O_{13}:Eu^{3+}$ phosphors at 570, 583, 615, 652, and 704 nm, respectively. The peaks observed at 580 to 600 nm are due to the magnetic dipole transition of Eu^{3+} ions. The emission peak at 615 nm wavelength is ascribed to the electric dipole transition $^7D_0 \rightarrow ^7F_2$ [13]. The sol-gel method produced the most dominant emission peak, compared to other methods, implying efficient energy transfer from the host to the dopant, the most dominant peak at 614 nm wavelength is attributed to the $^5D_0 \rightarrow ^7F_2$ transition of the dopant.

3.4 CIE color coordinates

The Commission Internationale de l'Eclairage (CIE) chromaticity diagram for $Zn_4B_6O_{13}:1 \text{ mol}\%Eu^{3+}$ phosphors prepared by three methods are shown in Fig. 4. The CIE chromaticity coordinates are in the form of (x, y) and were used for the analysis of the emission colours. The estimated CIE colour coordinates for $Zn_4B_6O_{13}:Eu^{3+}$ are as follows: (0.642, 0.353) sol-gel method, (0.641, 0.352) combustion method, and (0.644, 0.354) solid state method. All the obtained emissions fall within the red region of the CIE chromaticity diagram, which indicates efficient incorporation of Eu^{3+} ions into the host as it is known for its red emissions. The energy transitions shown in Figure 3 (b) are responsible for the red colour emission. This implies that these $Zn_4B_6O_{13}:Eu^{3+}$ phosphors are potential candidates for application in tuneable red light-emitting diodes [14]. The prepared samples were analysed at an excitation wavelength of 246 nm.

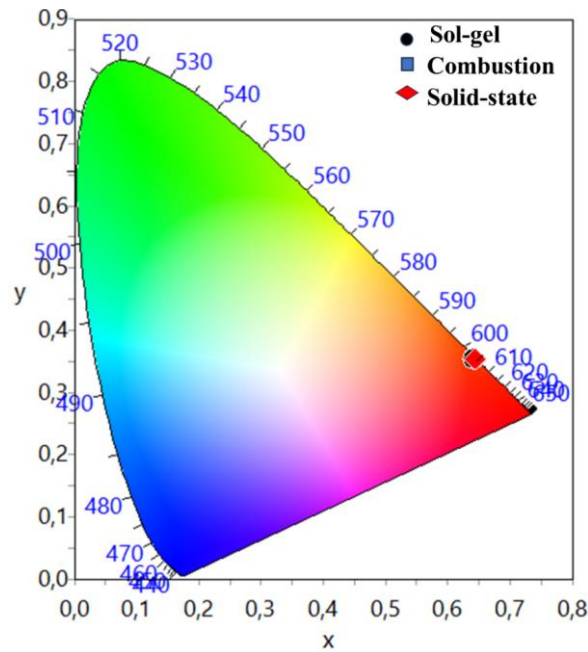


Figure 4. CIE colour diagram of $Zn_4B_6O_{13}:xEu^{3+}$ (where $x = 1\%$) nanophosphors prepared by: Sol-Gel, Combustion, and Solid-state reaction synthesis method.

Table 2. CIE colour co-ordinates of $Zn_4B_6O_{13}:xEu^{3+}$ (where $x = 1\%$) nanophosphors prepared by various chemical techniques: (1) Sol-Gel (2) Combustion and (3) Solid-state reaction method.

Sample No	Sample	CIE-coordinates
1	$Zn_4B_6O_{13}:Eu^{3+}$ (Sol-gel)	(0.642, 0.353)
2	$Zn_4B_6O_{13}:Eu^{3+}$ (Combustion)	(0.641, 0.352)
3	$Zn_4B_6O_{13}:Eu^{3+}$ (Solid-state)	(0.644, 0.354)

Conclusion

Eu³⁺ doped Zn₄B₆O₁₃ phosphors were successfully prepared by the sol-gel, combustion, and solid-state synthesis methods. The XRD results confirm the cubic structure of Zn₄B₆O₁₃:Eu³⁺ in all synthesis methods. The incorporation of Eu³⁺ into Zn₄B₆O₁₃ phosphors did not affect the crystal structure of the sample. Hexagonal, cubic, and some irregular agglomerated morphologies were observed in SEM images. At 900 °C annealing temperature caused some particles to be more adherent. The samples prepared were excited at different wavelengths of 246. The PL emissions spectra show characteristic emissions of Eu³⁺ from its ⁵D₀ level to ⁷F_j where j = 1, 2, 3, and 4. The high-intensity peak was observed at 614 nm excitation wavelength. The CIE chromaticity diagram revealed that all the prepared Zn₄B₆O₁₃:Eu³⁺ phosphors produced red colour emissions. All Eu³⁺ doped Zn₄B₆O₁₃ phosphors show excellent emission properties to be used for the fabrication of tunable-red LEDs.

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