

Role of Zinc Ions in Europium Doped Zinc Aluminate Phosphor

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ABSTRACT

The demand for efficient, reliable, and high-performance phosphor materials in solid-state lighting and optoelectronic devices has led to significant research into various doped semiconductor materials. One of the most difficult issues in this field is improving the luminous characteristics and structural stability of these materials. This study focuses on the optical and structural characteristics europium (Eu^{2+}) doped zinc aluminate (ZnAl_2O_4) doped with different zinc ion concentrations. All the samples were prepared by using urea as the fuel and the combustion method with chemical balance of: $3\text{Zn}_{(1+x)}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 6\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + 20\text{CH}_4\text{N}_2\text{O} + 1.0 \text{ mol\% Eu}(\text{NO}_3)_3 + x\text{Zn}(\text{NO}_3)_2 = 3\text{Zn}_{(1+x)}\text{EuAl}_2\text{O}_4 + 20\text{CO}_2 + 112\text{H}_2\text{O} + 32\text{N}_2$. The Eu^{2+} concentration was constant at 1.0 mol%, while zinc ions values varied from 1.0 mol% to 1.8 mol%. Combustion was carried out with temperature of 600°C , phosphors were converted from liquid to fine white nanoparticles. All the samples were characterized using the X-ray diffraction (XRD) method, photoluminescence (PL) spectroscopy, and ultraviolet-visible (UV-Vis) spectroscopy. The XRD patterns showed consistent peak positions and sharp diffraction peaks, indicating high crystallinity and phase purity of the synthesized samples. Photoluminescence analysis revealed that the highest emission intensity occurred at a zinc concentration of 1.2 mol% after excited with 350 nm. The CIE 1931 analysis indicated that europium-doped zinc aluminate emitted warm yellowish-red light with correlated color temperature (CCT) values ranging from 2145 K to 2702 K. Furthermore, UV-Vis spectroscopy analysis showed major UV absorption around 200 nm for all samples, gradually decreasing towards the visible region. The sample with 1.8 mol% of zinc concentration exhibited the highest UV absorbance, while pure ZnAl_2O_4 displayed the lowest.

Keywords: Zinc aluminate; europium doping; combustion synthesis; X-ray diffraction (XRD); photoluminescence (PL)

INTRODUCTION

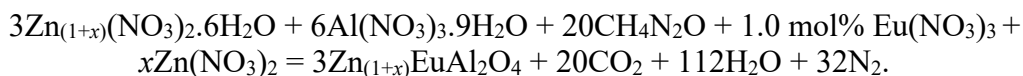
Nanoparticles are fundamental in the fabrication of nanostructures and are vital in the field of nanotechnology. Over the past century, this research field has made major advancements, particularly in recent decades [1-3]. However, the research also highlighted issues in improving the luminous properties of nanophosphors because of the compaction of the porous nanophosphor layer and the non-radiative decay time of typical phosphors [4-5].

In this study, the zinc aluminate, ZnAl_2O_4 was chosen as the host of nanophosphor. Zinc aluminate is also known for its high luminescence efficiency and stability, making it an excellent host material for solid-state lighting applications [6-13]. Till now, many researchers have attempted to produce Eu doped ZnAl_2O_4 phosphors using a variety of chemical methods [14-16]. However, thorough studies on the effect of zinc ions of europium doped zinc aluminate spinel on structural, optical, luminescent, and decay curve properties have not been studied in detail.

To the best of our knowledge, less reports exist on the synthesis of europium doped ZnAl_2O_4 phosphors with varying zinc ion concentrations using the combustion method. In this study, pure zinc aluminate and five series of 1 mol% europium-doped zinc aluminate with varying zinc ion concentrations (1.0, 1.2, 1.4, 1.6, and 1.8 mol%) were prepared using combustion synthesis. The main focus of this work is to understand the effect of increasing zinc ion concentration on europium-doped zinc aluminate. The structural studies of ZnAl_2O_4 with doped Eu^{2+} ions of prepared samples are verified using X-ray Diffraction. Lastly, this study aims to attain knowledge on how different concentrations of zinc ions affect the optical properties of ZnAl_2O_4 phosphor.

MATERIALS AND METHODS

Six samples of europium doped ZnAl_2O_4 were prepared, consisting of one pure zinc aluminate and five with varying zinc ion concentrations (0 mol%, 0.2 mol%, 0.4 mol%, 0.6 mol%, and 0.8 mol%) with constant concentration of europium at 1 mol%. The chemical equations for each are outlined accordingly. The basic reaction for pure ZnAl_2O_4 precursor: $3\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 6\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + 20\text{CH}_4\text{N}_2\text{O} = 3\text{ZnAl}_2\text{O}_4 + 20\text{CO}_2 + 112\text{H}_2\text{O} + 32\text{N}_2$. However, the basic reaction for europium doped ZnAl_2O_4 precursor:



Europium oxide was dissolved in the nitrate precursor and stirred at 70 °C on a magnetic stirrer at 400 rpm for 30 min. Then, aluminum nitrate nano-hydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and zinc nitrate hexahydrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to the mixture. Urea was included and stirred for another 30 minutes until a clear solution formed. This solution was heated in a furnace at 600 °C for 9 min, producing fluffy zinc aluminate phosphor, which was then ground into a fine powder. The samples were characterized using the X-ray

diffraction (XRD), photoluminescence (PL), and ultraviolet-visible (UV-Vis) spectroscopy.

RESULTS AND DISCUSSION

Six samples of nano-powder phosphorus were prepared for this study consist of a pure ZnAl_2O_4 with no dopants and five series of europium doped ZnAl_2O_4 of addition different concentration of zinc ions which are 0 mol%, 0.2 mol%, 0.4 mol%, 0.6 mol% and 0.8 mol% doped with 1 mol% europium ion. The samples produced through the combustion synthesis are of white powder form. Upon closer inspection, the powders appear slightly yellowish in color as shown in Figure 1.

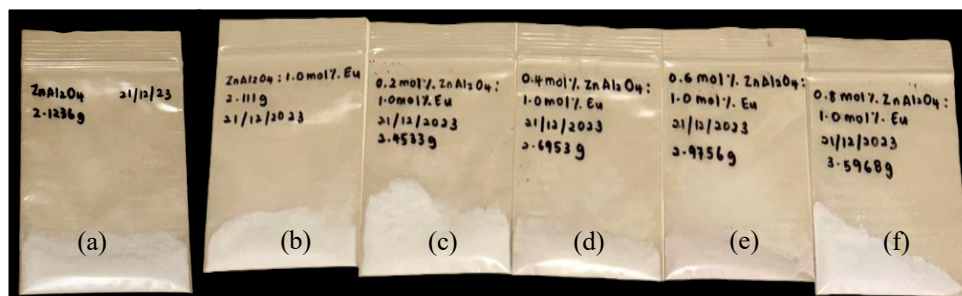


Figure 1. Six samples of nano-powder phosphorus prepared

X-ray Diffraction

Figure 2 represents the XRD patterns of pure ZnAl_2O_4 and different concentration of zinc ion at 1.0, 1.2, 1.4, 1.6 and 1.8 mol% doped with 1 mol% Eu. The patterns show a consistent peaks where the highest intensity of peak is located near 40° for all the samples with uniform location of all other peaks of lower intensity. The existence of sharp, well-defined peaks shows the exceptional crystallinity of the produced materials. By Match3 Crystal Impact Software, the XRD peaks produced was compared with standard database, this study confirmed that all samples were 100% gahnite (ZnAl_2O_4). Gahnite is notable for having a cubic crystal structure. The unit cell parameters were found to be $a = b = c = 8.0832 \text{ \AA}$. This value is similar to the theoretical value for gahnite, 8.084 \AA , as reported in prior studies [5].

The crystallite size of the sample was determined by calculated using Scherrer's equation and Williamson and Hall (W-H) plot as summarized in Table 1. It shows that, the higher concentration of zinc the smaller the size of crystal produced. The higher the concentration of zinc ion used, the lower the intensity of XRD peaks. This led to higher strain value and smaller size of the crystallite size. From XRD pattern analysis, the presence of Zn ion has modified the crystal structure, size and the micro-strain of the samples.

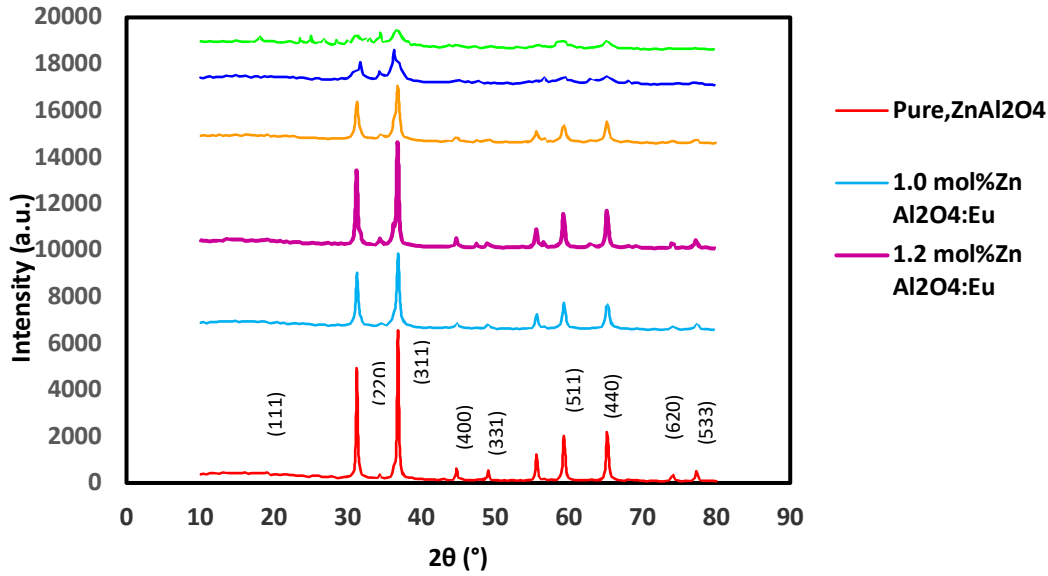


Figure 2. X-ray diffraction (XRD) patterns of pure $ZnAl_2O_4$ and x mol% $ZnAl_2O_4:1\text{mol\% Eu}$ ($x=1.0, 1.2, 1.4, 1.6, 1.8$)

Table 1. Values of microstrain, y-intercept and crystallite size from W-H plot and Scherrer equation.

Sample Name	Micro-strain, ϵ	y-intercept	Crystallite size, D (nm)	
			W-H Plot	Debye-Scherrer
$ZnAl_2O_4$	$7.23 \times 10^{-4} \pm 6.55 \times 10^{-4}$	0.00395	35.10	23.82
1.0 mol% $ZnAl_2O_4:1$ mol% Eu	$5.03 \times 10^{-4} \pm 0.00303$	0.00564	24.58	14.22
1.2 mol% $ZnAl_2O_4:1$ mol% Eu	$0.00134 \pm 9.87 \times 10^{-4}$	0.00389	35.64	20.72
1.4 mol% $ZnAl_2O_4:1$ mol% Eu	0.00231 ± 0.0028	0.00516	26.87	34.02
1.6 mol% $ZnAl_2O_4:1$ mol% Eu	0.00249 ± 0.00729	0.02000	6.93	5.27
1.8 mol% $ZnAl_2O_4:1$ mol% Eu	0.06426 ± 0.05335	0.01864	7.44	4.42

Glowing Emission of Photoluminescence Spectroscopy (PL)

Figure 3 displays the glowing emission for phosphor europium doped $ZnAl_2O_4$ doped with 1.0 mol% concentration of Eu^{2+} ions and 1.0, 1.2, 1.4, 1.6 and 1.8 %mol of zinc ions under an excitation of wavelength of 350 nm. The summarized of image analysis for red, green and blue (RGB) distribution as is shown in Table 2. Sample with 1.2%mol gives the highest value of RGB then more white in color compared to others. By additional of more Zn ions, the value of red and green color increased.

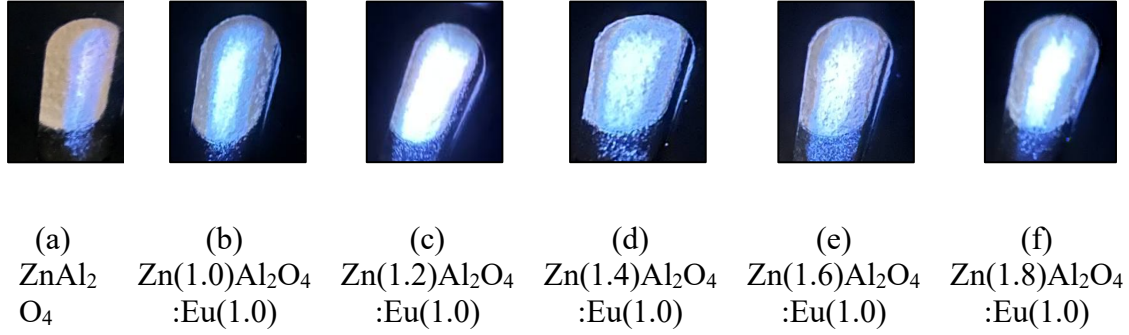


Figure 3. Emission color of pure (a) ZnAl₂O₄ and (b) to (f) x mol% ZnAl₂O₄:1mol% Eu ($x = 0, 0.2, 0.4, 0.6, 0.8$) (from left to right, respectively)

Table 2. The RGB distribution of image analysis

Sample	Red	Green	Blue	Average
Pure, ZnAl ₂ O ₄	178.61	189.72	242.58	203.63
1.0% ZnAl ₂ O ₄ :Eu	200.78	238.55	251.02	230.11
1.2% ZnAl ₂ O ₄ :Eu	253.43	254.78	254.33	254.36
1.4% ZnAl ₂ O ₄ :Eu	215.32	251.56	251.53	239.48
1.6% ZnAl ₂ O ₄ :Eu	233.29	248.95	250.78	244.36
1.8% ZnAl ₂ O ₄ :Eu	243.34	251.54	253.61	249.57

Photoluminescence Spectroscopy (PL)

The PL emission spectra of europium doped zinc aluminate for different concentrations zinc ions under UV excitation of wavelength of 350 nm is shown in Figure 4. The europium doped zinc aluminate emit the broad spectrum from 480 to 680 nm with three dominant peaks as 558 nm, 601 nm and 638nm. Without the presence of europium ion, the pure sample of ZnAl₂O₄ also shows a broad emission spectrum. With the presence of europium ion in the sample, extra peaks at 601 nm and 638 nm were more dominant with 1.2 mol% zinc ion sample exhibited the highest emission intensity, whereas the sample with 1.8 mol% zinc ion showed the lowest intensity. Quenching concentration was observed at higher concentration. The phenomenon of rare-earth ions quenching is explained by the non-radiative energy transfer between activator ions, which occurs by interactions such as exchange interactions and multipole interactions [6].

Future analysis of PL emission spectrum was carried out with CIE 1931 and correlated color temperature (CCT). Table 3 shows that europium doped zinc aluminate emits yellowish-red color with a Correlated Color Temperature (CCT) values ranging from 2145 K to 2702 K based on the CIE coordinates. Based on the CIE coordinates also, the CIE 1931 diagram was plotted and coordinate shows that the light emitted is warm, typical of materials doped with europium, which tends to shift emission towards the red part of the spectrum.

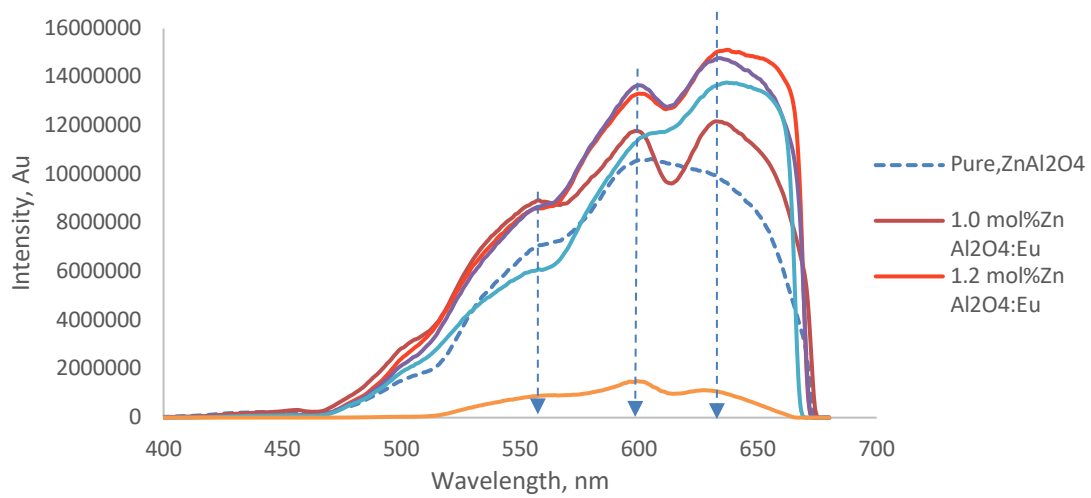


Figure 4. Emission spectra of $x\text{mol}\% \text{ZnAl}_2\text{O}_4:1\text{mol}\% \text{Eu}$ ($x = 1.0, 1.2, 1.4, 1.6, 1.8$)

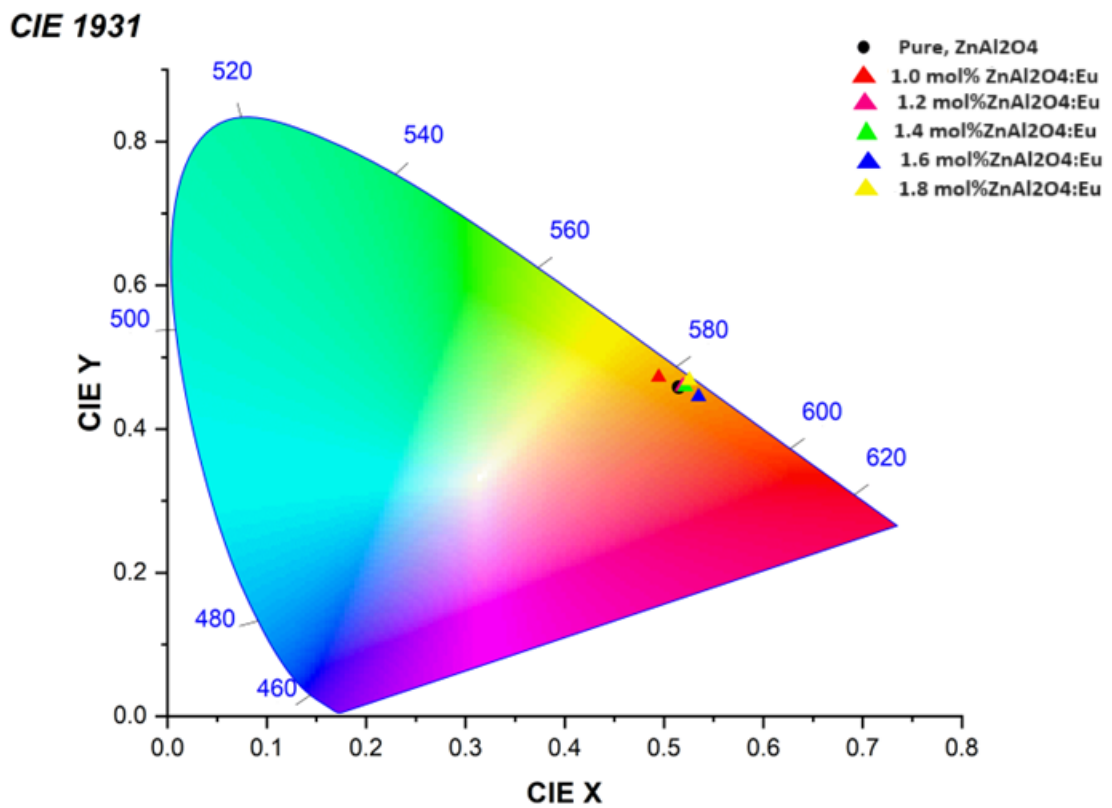


Figure 5. CIE 1931 plot of $x \text{ mol}\% \text{ZnAl}_2\text{O}_4:1\text{mol}\% \text{Eu}$ ($x = 0, 0.2, 0.4, 0.6, 0.8$)

Table 3. CIE Coordinates and CCT values of each sample

Sample Name	CIE Coordinate		CCT (K)
	(x,y)		
	x	Y	
Pure, ZnAl ₂ O ₄	0.51473	0.45843	2405
1.0 mol% ZnAl ₂ O ₄ :1 mol% Eu	0.49465	0.47223	2702
1.2 mol% ZnAl ₂ O ₄ :1 mol% Eu	0.51894	0.45958	2372
1.4 mol% ZnAl ₂ O ₄ :1 mol% Eu	0.51894	0.45878	2343
1.6 mol% ZnAl ₂ O ₄ :1 mol% Eu	0.53478	0.44517	2145
1.8 mol% ZnAl ₂ O ₄ :1 mol% Eu	0.52535	0.46776	2365

UV-Vis Spectroscopy

For UV-Vis Spectroscopy as shown in Figure 6, showed that 1.8 mol% Zn sample exhibits the highest absorbance at 200 nm but with a sudden drop around 250 nm while pure ZnAl₂O₄ sample had the lowest UV absorbance. In comparison, the 1.0 mol% Zn sample, which is ZnAl₂O₄ doped with 1 mol% europium but without additional zinc ions, has a higher absorbance than pure ZnAl₂O₄, but a lower absorbance than the 0.2, 0.4, 0.6, and 0.8 mol% Zn samples. All samples show the highest absorbance at around 200 nm. This indicates strong absorption in the UV region, which is typical for materials with electronic transitions from the valence band to the conduction band. As the wavelength increases from 200 nm to 400 nm, the absorbance gradually decreases in all samples. Beyond 400 nm, the absorbance decreases to zero, suggesting minimal absorption in the visible region.

The Tauc plots of all samples were generated based on the UV-Vis analysis, and the energy bandgaps were extrapolated from them. Figure 7 shows the direct bandgap energy value for pure zinc aluminate sample. Table 4 lists the values of direct and indirect energy band gaps for pure ZnAl₂O₄ and ZnAl₂O₄:Eu_(1.0) at different zinc concentrations (1.0, 1.2, 1.4, 1.6, and 1.8 mol%). The pure ZnAl₂O₄ sample has a typical band gap value that matches existing research, proving its semiconductor properties. Adding europium without zinc causes the indirect band gap to decrease while slightly raises the direct band gap. This means that europium ions alter the electronic structure, perhaps introducing new electronic states inside the band structure. Both direct and indirect band gaps dramatically increase at the highest concentration of zinc, which is 1.8 mol%. This notable change shows how high zinc concentrations affect the crystal structure and electrical properties, perhaps widening the band gap.

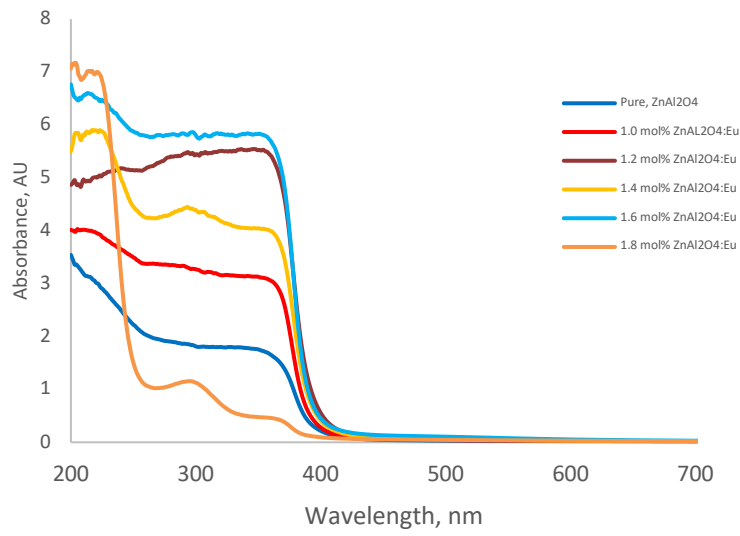


Figure 6. Absorbance (a.u.) vs wavelength (nm) plot for UV-Vis spectra analysis

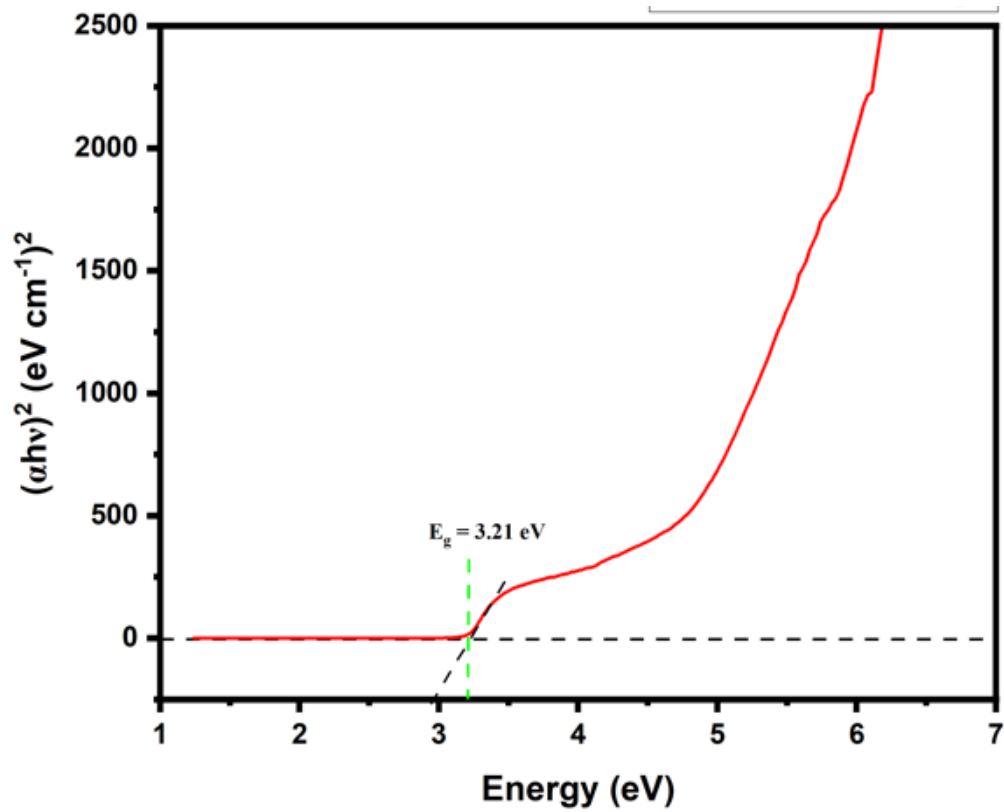


Figure 7. Tauc plot for Pure ZnAl₂O₄

Table 4. Direct and indirect energy band gap (eV) of samples

Sample 1	Energy Band Gap (eV)	
	Direct	Indirect
Pure, ZnAl ₂ O ₄	3.21	2.87
1.0 mol% Zn Al ₂ O ₄ : 1 mol% Eu	3.22	2.78
1.2 mol% Zn Al ₂ O ₄ : 1 mol% Eu	3.14	2.79
1.4 mol% Zn Al ₂ O ₄ : 1 mol% Eu	3.21	2.81
1.6 mol% Zn Al ₂ O ₄ : 1 mol% Eu	3.22	2.77
1.8 mol% Zn Al ₂ O ₄ : 1 mol% Eu	4.96	3.00

CONCLUSION

A series of europium doped zinc aluminate phosphor samples with addition of zinc at 0, 0.2, 0.4, 0.6 mol% zinc ion and 1 mol% europium has been successfully prepared using a urea-fueled combustion process for about 9 min at 600 °C. Based on the experimental evidence, it was found that, different concentration of zinc ion affects the optical and structural properties. X-ray diffraction patterns confirms the presence of sharp, well-defined peaks indicated the outstanding crystallinity of the materials produced. Furthermore, the determination of optical properties was supported by photoluminescence (PL) analysis. The result shows the highest emission intensity occurs at 1.2 mol% zinc. Meanwhile, the result from UV-Vis analysis shows that the highest UV absorbance is observed at 1.8 mol% zinc, while the lowest is in pure ZnAl₂O₄. This shows that doping with both zinc and europium enhances UV absorption more effectively than europium alone, especially at higher zinc levels. The Tauc plot analysis shows that zinc content affects the band gaps of zinc aluminate. Pure ZnAl₂O₄ has typical band gap values suitable for optoelectronic applications.

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