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Paper Authors

R. VENKATESH, N. DHANANJAYA, G. NAGARAJU, UDAYA BHANU



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RARE EARTH ACTIVATED AND SENSITIZED GREEN SYNTHESIS OF ZINC ALUMINATE FOR DISPLAY APPLICATIONS

¹R. VENKATESH, ²N. DHANANJAYA, ³G. NAGARAJU, ⁴UDAYA BHANU

¹PG Scholar, Department of Physics, Bharathi University.

²Assistant professor (Ph.D), Dept of Physics, BMSIT, Bangalore.

³Assistant professor (Ph.D), Dept of Chemistry, SSIT, Tumakuru.

⁴PG Scholar, Dept of Chemistry, SSIT, Tumakuru.

ABSTRACT

The Nano regime of Zinc aluminate ($ZnAl_2O_4$) and trivalent doped Zinc aluminate nanoparticles was synthesized by green combustion technique. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and Aluminium nitrate ($Al(NO_3)_3$), were used as starting materials. Naturally available Euphorbia Resinifera latex of *E-tirucalli* family was used as a combustion agent. Dysprosium nitrate was used as co-dopant. The as formed samples were calcined at $900^{\circ}C$ for 3 h. The synthesized samples were characterized for their structural and optical investigations using X-ray diffraction (XRD) analysis and Photoluminescence (PL). The size of the particle was calculated by Scherer equation and Williamson hall equation using XRD pattern. Purity of the sample was tested by Fourier Transform Infrared spectroscopy (FTIR). The optical property like band gap was determined by UV-Visible spectra and luminescent characteristic of red and enhanced emission from RE ion were observed by PL which was used in WLED applications.

KEYWORDS Resinifera latex, Rare earth, Xray diffraction, aluminates, WLED

1.INTRODUCTION

Recent trend in Nano crystalline particles have been given much interest because of their size dependent properties as well as technological. This can be achieved easily using the concept of quantum confinement phenomena and surface to volume ratio by triggered in grain size, leading to unusual and interesting optical, electrical, mechanical and magnetic properties which is unknown in the bulk material[1]. New applications of Nano scale phosphors include integrated optics, electroluminescent devices, luminescent fillers in transparent matrices (glass or plastics) and biomedical applications such as optical imaging and

phototherapy [2,3]. Hence, it is very important to study high quality phosphors operating under UV excitation for better performance of such LEDs. The properties of these materials arise from complex interactions among the host structure, activators, and defects, which are strongly dependent on the composition. Rare earth ions are widely used as activators or sensitizers in different hosts due to their high fluorescence efficiencies. In continuation $ZnAl_2O_4$ was used as one of the important phosphor host material for the display applications and optical stress sensors. The band gap energy of polycrystalline $ZnAl_2O_4$

(3.8 eV) indicates the material is transparent for light possessing wavelengths. Thus, ZnAl₂O₄ can be used for ultraviolet (UV) photo electronic devices [4], high stability and high mechanical strength [5, 6]. The film of these composites with outstanding optical transmittance [7] have been utilized in a wide variety of applications including electric transducers [8], gas sensors [9], window layers and anti-reflection solar cells [10]. The bulk of these composites with opaque white colour may hold the potential applications of optical and thermal resistance. The efficiency of the host material can be enhance by doped with rare earth metal ions have been investigated due to its luminescent properties. This properties results from its stability and high emission quantum yields [11, 12]. In this manuscript, we have reported the synthesis of nanocrystalline trivalent doped and co-doped ZnAl₂O₄:Eu³⁺:Dy³⁺ by green combustion method.

2. EXPERIMENT

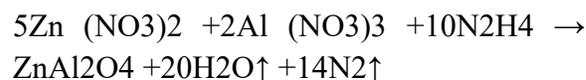
2.1 CHEMICALS

The purity and manufacturing of the chemicals used for the preparation of ZnAl₂O₄, ZnAl₂O₄:Eu, ZnAl₂O₄:Eu³⁺:Dy³⁺ are as follows. Zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O, purified], Aluminium nitrate nonahydrate [Al(NO₃)₃·9H₂O, extra pure], Eu(NO₃)₃, Dysprosium (III) nitrate pentahydrate [Dy(NO₃)₃·5H₂O, 99.9% pure], were procured from Aldrich company.

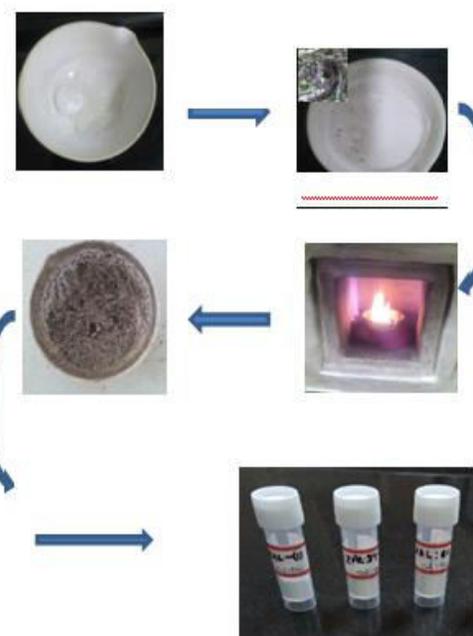
2.2 SAMPLE PREPARATION

The solution combustion method was used to synthesis these Nano phosphors. Zinc nitrate and Aluminium Nitrate are taken with desired amount in a Petridish. The

compound were heated by dissolving in distilled water on a sand bath for about 10-15 minutes until the compound becomes to gel form. Then the desired amount of dopant was added to the petridish containing gel. Naturally extracted fuel of Euphorbia Resinifera latex is taken for combustion. The solution was heated at 300 °C in a pre-heated furnace to get porous products. Since in this method samples are prepared through the solution combustion route, better control over sample homogeneity and particle size would be obtained by dehydration followed by decomposition generating combustible gases. After complete combustion, the petridish is taken out from the furnace and is calcined in the furnace for about 900°C for three hours. The prepared sample then subjected to different characterization to study the said applications. The combustion reaction indicated is as follows:



2.3 SYNTHESIS MECHANISM



3. RESULTS AND DISCUSSIONS

3.1 X-RAY DIFFRACTION

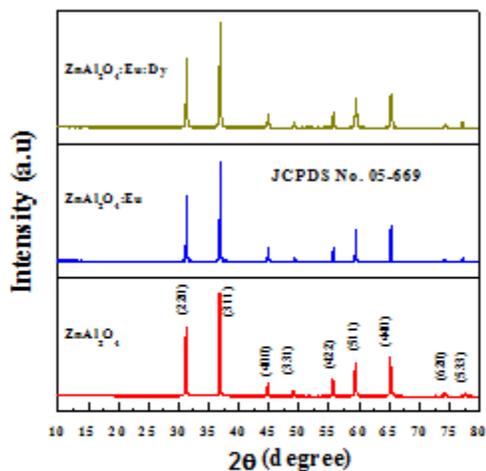


Fig. 1. X-ray diffraction spectra of synthesized $ZnAl_2O_4$ nanoposphor.

Figure 1 shows the XRD spectra of $ZnAl_2O_4:RE$ ($RE=Eu^{3+}:Dy^{3+}$) 1mol % nanoparticle. The intensity and angle (2θ) at which diffraction takes place gives the idea size and shape the nanoparticle. From the figure 1, it was clear that the prepared sample was cubic in nature with a space group $Fd-3m$ having inter planar distance $a = 8.0848$ also, the diffraction peaks originate at 2θ are close to the reported data for $ZnAl_2O_4$ (JC-PDS card 05-0669). The particle size was estimated using Scherer equation was found to be 16-20nm range also, this is in good agreement with size calculated with W-H plot (Figure 2). Addition of dopant or co-dopant to the lattice shows the variation in the broadening of the diffracted peaks undergoes distortion as revealed by the broadening of diffraction peaks. The particle size calculated for the synthesized samples from both Scherer and W-H method (figure.2) were tabulated in Table-1.

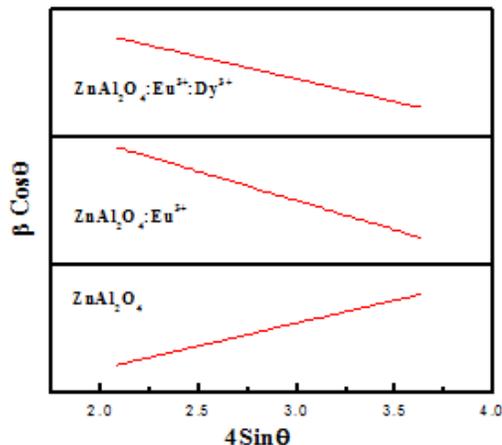


Fig. 2. W-H plot of synthesized $ZnAl_2O_4$ nanoposphor.

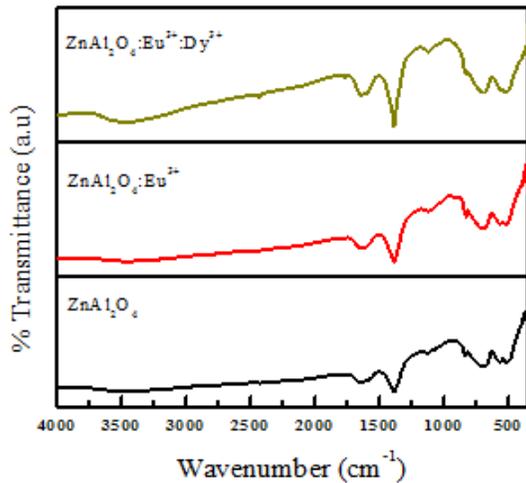
Sample	Crystallite size 'D' (nm)	
	Scherrer's	W-H Plot
$ZnAl_2O_4$	18.67	13
$ZnAl_2O_4:Eu^{3+}$	17.88	10
$ZnAl_2O_4:Eu^{3+}:Dy^{3+}$	17.88	10

Table 1. Estimated crystallite size values of

$ZnAl_2O_4:RE$ ($RE=Eu:Dy$) nanoposphor.

3.2 FOURIER TRANSFORM INFRARED SPECTRA

Purity and the functional that are associated with the samples are checked by FTIR spectra (Figure 3). From the figure it was observed that the three bands which are observed in the range $400-700cm^{-1}$ are characteristics of zinc aluminate. The bands at $657 cm^{-1}$ and $549 cm^{-1}$ are due to symmetric stretching and bending modes of AlO_6 and the band at $484 cm^{-1}$ is due to asymmetric stretching mode of AlO_6 group [13]. A broad peak around $3500 cm^{-1}$ may be attributed to the stretching and bending vibrations water molecules.



3.3 UV-VISIBLE ABSORPTION SPECTRA

Figure 4. Corresponding to UV-Vis absorption spectra of the synthesized samples. The direct band gap energy was calculated by the absorption coefficient given by Tauc equation $(\alpha hv)^2 = B(hv - E_g)^n$, where E_g is the energy gap, α is absorption coefficient, B is a constant and $h\nu$ is photon energy. The band gap energy was calculated by considering the wavelength directly and varies from 3.3-3.8 eV.

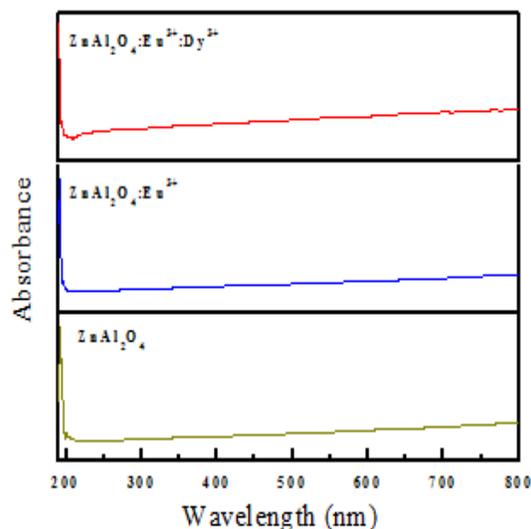


Fig. 4. UV-Visible absorption spectra of synthesized $ZnAl_2O_4$ nanophosphor.

3.4 PHOTOLUMINESCENCE SPECTROSCOPY

Figure 5. depicts the emission spectra of the rare earth doped and co-doped Nano phosphor excited at 330nm

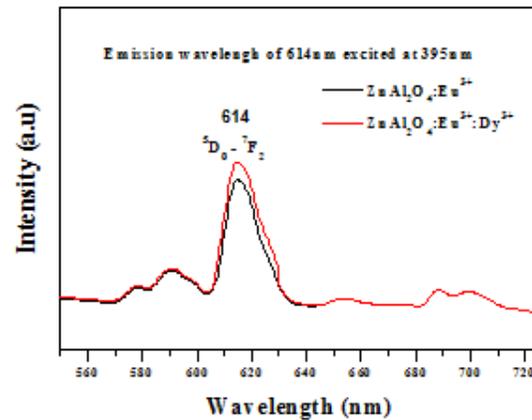


Fig. 5. PL spectra of synthesized nanophosphor.

The PLE emission intensity for $ZnAl_2O_4:Eu^{3+}$ and $ZnAl_2O_4:Eu^{3+}:Dy^{3+}$ transition from $^5D_0 - ^7F_J$ emission bands. Where $J=0,1,2$, refers to barrier energy and can be determined from the emission band of Eu^{3+} transitions. In luminescence transition bands there will be both magnetic dipole transition due to non-inversion symmetry of dopant ion and electric dipole transitions due to inversion symmetry occupation of dopant ion. For Eu^{3+} doped sample $^5D_0 - ^7F_1$ transition is due to magnetic dipole transition, which is independent of the host material. Whereas $^5D_0 - ^7F_2$ transition shows the strongest emission at 614nm excited at 395nm which is characteristic feature of Eu^{3+} ion, suggesting the chemical environment around Eu^{3+} ions is in low symmetry. Further, it was observed that for $ZnAl_2O_4:Eu^{3+}:Dy^{3+}$ sample there will be an enhancement in the intensity due to Dy^{3+} co-doped ion which distorts the crystal field surrounding

Eu³⁺ ion. From this spectra it was confirmed that emission is purely at red region of the spectra. Therefore it can be used as red component in WLED and many other display applications.

3.5 CIE color chromaticity

Phosphor	CIE 1931 coordinates		CIE1976 coordinates		CCT
	x	y	U'	V'	
ZnAl ₂ O ₄ :Eu ³⁺	0.3445	0.2949	0.2356	0.4537	4781
ZnAl ₂ O ₄ :Eu ³⁺ :Dy ³⁺	0.3408	0.2935	0.2334	0.4523	4983

Table 2. Shows CIE coordinates and CCT values for the prepared nanophosphor

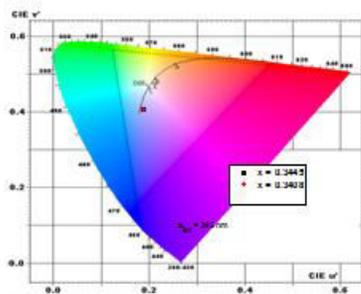


Fig. 6. CIE chromaticity

For practical lighting applications color quality was specified in terms of 1931 Commission International de l'Eclairage (CIE) chromaticity color coordinates. CIE coordinates (x, y) were calculated using PL data. The CCT 4781 K and 4983 K for excitation wavelength of 395 nm was obtained by transforming the (x,y) coordinates of the light source to (U', V') by using the equations

$$U' = 4x / (-2x + 12y + 3) \quad \text{and} \quad V' = 9y / (-2x + 12y + 3)$$

and by determining the temperature of the closest point of Planckian locus to the light source on the (U', V') uniform chromaticity diagram. CCT value for the prepared nanophosphors lower than 5000 K indicates the cold white light used for commercial

lighting purpose and higher than 5000 K indicates the warm white light used for home appliances

4.CONCLUSION

Easy method for the synthesis of doped and co-doped ZnAl₂O₄:RE (RE=Eu³⁺:Dy³⁺) Nano phosphors using green combustion technique by using euphorbia Resinifera as fuel has been established. Crystallite powders having small crystallite size of 16-20nm were obtained at 300°C for about 15 min of heating also by calcinating around 12000C for 3 h. PL results in emission around 614nm renders to red component in WLED. This Nano phosphor also finds use in solid state display applications, gas sensors, photo electronic devices and solar cells.

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