

# Bio-inspired synthesis and morphological studies of various dopants on Zinc Aluminate

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**Abstract:** ZnAl<sub>2</sub>O<sub>4</sub>:Tb<sup>3+</sup> (0.25 - 5 mol%) nanophosphor was synthesized by ultrasound assisted sonochemical route using bio-sacrificial Aloe Vera (A.V) gel as a template. The effect of sonication time, AV gel concentration, pH value, sonication power and temperature on the morphologies of the prepared samples were systematically explored and discussed. Probable formation mechanism for various morphologies of ZnAl<sub>2</sub>O<sub>4</sub>:Tb<sup>3+</sup> nanophosphor was discussed. Core-shell SiO<sub>2</sub>@ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup> (5 mol%) nanophosphor (NP) with coatings upto the level IV has been prepared by a facile solvothermal route, followed by heat treatment. Its morphological studies were discussed and it was found that the thickness of the shell increased with increase in coating cycles. Alkali metal ions (M<sup>+</sup> = Na, Li, K) co-doped ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup> (5 mol%) (ZAE) nanopowders (NPs) were prepared via solution combustion route using mimosa pudica leaves extract as a fuel. PXRD results of co-doped samples enhance the crystallinity and grain growth.

**Keywords:** Bio-inspired synthesis, Core-shell, Alkali – metal ions, Nanophosphor

## 1. INTRODUCTION

The rare earth (RE<sup>3+</sup>) ions doped inorganic nanomaterials have wide range of applications due to its unique properties such as high thermal stability, superior catalytic, electrical and optical properties [1,2]. Among the existing nanomaterials, the spinel Zinc aluminates (ZnAl<sub>2</sub>O<sub>4</sub>) have been preferred to be the better host in studying its properties in nanometric level due to its high thermal and chemical stability, high mechanical resistance, low acidity and hydrophobicity [3]. ZnAl<sub>2</sub>O<sub>4</sub> is a wide band gap semiconductor (E<sub>g</sub> = 3.8 eV) and they are attractive for the fabrication of superior nanophosphors due to their ease of preparation and chemical stability. The RE doped Zinc aluminates find wide range of technological applications in optoelectronics, sensors, flat-panel displays etc [4-6].

In the present work, a comparative morphological study of (i) ZnAl<sub>2</sub>O<sub>4</sub>: Tb<sup>3+</sup> (0.25- 5mol %) nanoparticles synthesized using bio-sacrificial A.V. template assisted ultrasound method, (ii) Core-shell SiO<sub>2</sub>@ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup> (5 mol%) nanoparticle (NP) prepared by a facile solvothermal method and (iii) Spinel ZnAl<sub>2</sub>O<sub>4</sub>: Eu<sup>3+</sup>, M<sup>+</sup> (M<sup>+</sup> = K, Na, Li) NPs synthesized by solution combustion route using mimosa pudica (MP) plant extract as fuel were studied.

## 2. EXPERIMENTAL METHODS OR METHODOLOGY

### 2.1 Synthesis of ZnAl<sub>2</sub>O<sub>4</sub>: Tb<sup>3+</sup> nanoparticle using ultrasound method

The novel ZnAl<sub>2</sub>O<sub>4</sub>: Tb<sup>3+</sup> (0.25 - 5 mol %) nanoparticle was synthesized by a bio-template A.V. gel assisted ultrasound method by using a high-intensity ultrasound horn with diameter of ~ 19 mm, with variable operating frequency. Stoichiometric amount of Zinc nitrate and Aluminium nitrate were dissolved in 100 ml distilled water and systematically mixed in a magnetic stirrer to get uniform solution. The stoichiometric amount of Terbium nitrate (0.25 - 5 mol %) and different concentration of A.V gel extracted from the inner gel portion of the A.V. leaves was added to above resultant solution slowly.

Then, the ultrasonic wave was introduced into the solution by maintaining the power of about 50 W, corresponding to the intensity of about 17.6 Wcm<sup>-2</sup> under ambient air at fixed temperature of 75° C and by varying ultrasonic time (1 - 6 hrs). The solution was kept undisturbed until a white precipitate was formed. The precipitate was filtered and washed thoroughly by using distilled water and ethanol. The obtained product was dried at 60° C for 3 hrs in a vacuum oven. Finally, the dried precipitate was grinded thoroughly into powder form [7-10]. Synthesis procedure is shown in Fig.1.

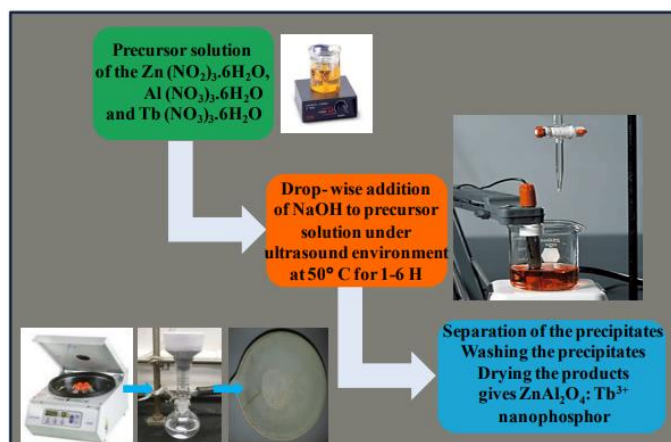


Fig.1 Schematic representation for the synthesis of  $ZnAl_2O_4: Tb^{3+}$  nanoparticle by sonication method

## 2.2 Synthesis of core $SiO_2$ and core-shell $SiO_2@ZnAl_2O_4:Eu^{3+}$ (5 mol%) nanoparticle

Mono disperse  $SiO_2$  spheres were synthesized by Stöber method. The detailed experimental procedure for the preparation of  $SiO_2$  was described elsewhere [11]. In a typical preparation process,  $Eu^{3+}$  doped  $ZnAl_2O_4$  NP were coated onto the as-prepared silica cores by a solvothermal method. In the first stage, 1 g of prepared silica spheres was dispersed in 60 ml of polyethylene glycol (PEG) and 1.95 ml of  $Zn(NO_3)_2 \cdot 6H_2O$  (1.0 M),  $Al(NO_3)_3 \cdot 9H_2O$  (1.0 M) and 1 ml of the  $Eu(NO_3)_3 \cdot 5H_2O$  (0.05 M) were added into the above mixture under constant stirring. Then, 1.5 g of polyvinyl pyrrolidone (PVP K30,  $M = 40,000$ ) was dissolved in the mixture thoroughly. Afterwards, 10 ml of ethanol solution containing 0.11 g of thiourea ( $SC(NH_2)_2$ ) was added drop wise into the above solution with vigorous agitation. Further, 1 ml of NaOH solution (2 M) was gradually added to the mixture as precipitating agent. After being stirred for another 1 h, the mixture was transferred to a 150 ml Teflon-lined autoclave and heated at 180 °C for 36 h. After that it was cooled to RT, the precursors were separated, washed and dried at 60 °C followed by calcined at 800 °C for 2 h. Step by step formation process of core-shell  $SiO_2@ZnAl_2O_4:Eu^{3+}$  (5 mol%) NP was shown in Fig. 2.



Fig.2 Schematic illustration for the formation process of  $SiO_2$  core and core-shell  $SiO_2@ZnAl_2O_4:Eu^{3+}$

## 2.3. Synthesis of $ZnAl_2O_4:Eu^{3+}$ , $M^+$ ( $M^+ = K^+, Na^+$ and $Li^+$ ) nanoparticles

Analar grade zinc nitrate hexahydrate ( $Zn(NO_3)_2 \cdot 6H_2O$  (98%)), aluminum nitrate ( $Al(NO_3)_3 \cdot 9H_2O$  (99.9%)), europium nitrate pentahydrate ( $Eu(NO_3)_3 \cdot 5H_2O$  (99.9%)), potassium nitrate ( $KNO_3$ ), sodium nitrate ( $NaNO_3$ ) and lithium nitrate ( $LiNO_3$ ) were used as starting materials. The MP leaves extract was used as a fuel. The extraction of MP is described elsewhere [12]. The stoichiometric quantities of reagents and MP extract (20 mL) were taken in a cylindrical Petri dish and dissolved well in double distilled water. Further, the reaction mixture was stirred well in magnetic stirrer for ~30 min. Later the Petri dish containing the mixture was introduced into a pre-heated muffle furnace maintaining at  $500 \pm 10$  °C. The resultant mixture underwent thermal dehydration with the liberation of large amount of gaseous product. The

whole process completes within ~5 min with voluminous powder product [13,14]. The obtained powder was calcined at ~800 °C for 3 h and used for various characterization. The schematic illustration for the combustion synthesis of  $ZnAl_2O_4:Eu^{3+}$ ,  $M^+$  ( $M^+ = K^+, Na^+$  and  $Li^+$ ) NPs is shown in Fig. 3.



Fig.3. Schematic diagram of combustion synthesis of  $ZAE:M^+$  ( $M^+ = K^+, Na^+$  and  $Li^+$ )

### 3. CHARACTERIZATION

Shimadzu X-ray diffractometer (PXRD-7000) using Cu-K $\alpha$  radiation ( $\lambda = 1.541 \text{ \AA}$ ) was used to study the crystalline purity and phase of prepared sample. Morphology, particle and crystallite sizes were examined by scanning electron microscopy (SEM, Hitachi-3000 model).

### 4. RESULTS AND DISCUSSION

#### 4.1 Morphological study of $ZnAl_2O_4:Tb^{3+}$ (3 mol %) nanoparticle

The PXRD patterns of un-doped and  $ZnAl_2O_4:Tb^{3+}$  (0.25– 5 mol%) nanoparticle was shown in Fig. 4.1. The obtained patterns exhibit cubic phase and were well indexed with JCPDS No. 82-1043 [15]. Fig.4.2 shows the SEM micrographs of  $ZnAl_2O_4:Tb^{3+}$  (3 mol %) nanoparticle synthesized with different ultrasound irradiation time (1–6 h). When ultrasound irradiation time was at ~1 h, spike-like structures begin on the surface was observed (Fig. 4(a)). When it was increased, small spikes undergo self-assembly and grow to form well-defined clear spike like structured with typical widths of ~20–45  $\mu m$ .

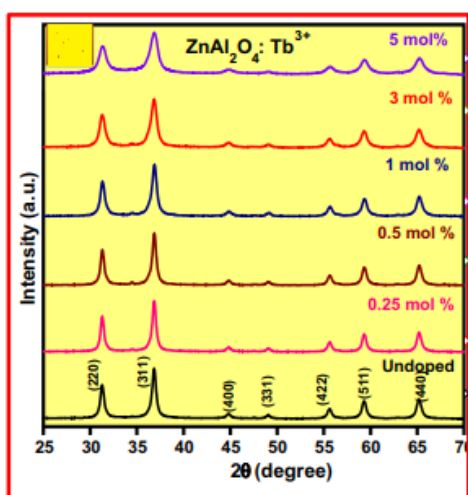


Fig.4.1. PXRD patterns of  $ZnAl_2O_4:Tb^{3+}$  NPs

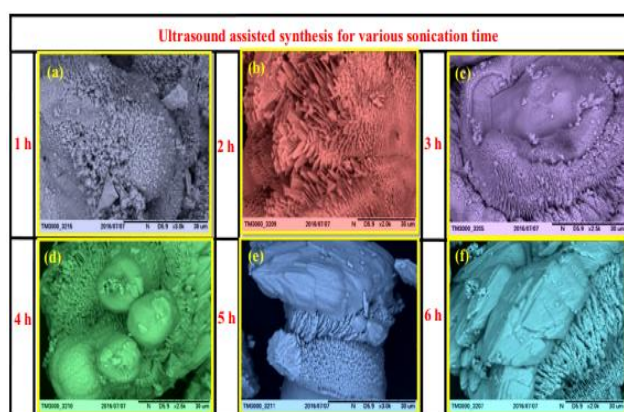


Fig.4.2. SEM images of  $ZnAl_2O_4:Tb^{3+}$  (3 mol%) nanopowder synthesized with different sonication time (1, 2, 3, 4, 5 and 6 h) with 20 ml A.V. gel concentration

#### 4.2 Morphological study of core-shell $SiO_2@ZnAl_2O_4:Eu^{3+}$ (5 mol%) nanoparticle

Fig. 5.1(a) shows the PXRD profiles of  $ZnAl_2O_4:Eu^{3+}$  (1–11 mol%) NP. All the recorded peaks were well assigned to pure cubic phase (JCPDS card No. 82-1043). Fig. 5.1(b) shows the PXRD patterns of  $ZnAl_2O_4:Eu^{3+}$  (5 mol%), pure  $SiO_2$  and core-shell  $SiO_2@ZnAl_2O_4:Eu^{3+}$  (5 mol%) NP along with a standard JCPDS card of  $ZnAl_2O_4$ . Fig.5.2 shows the SEM micrographs of (a) spherical  $SiO_2$  cores, (b)  $ZnAl_2O_4:Eu^{3+}$  (5 mol%) NP and (c-f) different layers (I–IV) of  $ZnAl_2O_4:Eu^{3+}$  (5 mol%) nanoparticle on spherical  $SiO_2$  core. From the figure, it was clear that the  $SiO_2$  cores were smooth, non-agglomerated and spherical in nature with different sizes. After functionalizing the  $SiO_2$  cores by

ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup> (5 mol%) NPs, the resultant SiO<sub>2</sub>@ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup> (5 mol%) nanoparticle was found to be agglomerated and marginally higher than the pure spherical particles owing to extra layers of ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup> on them.

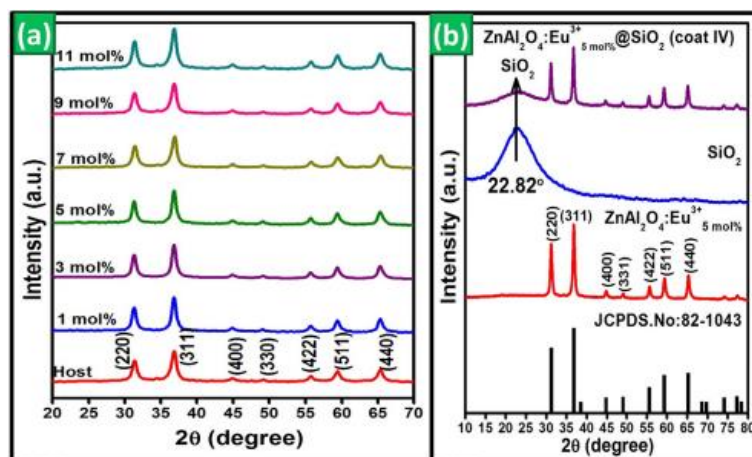


Fig.5.1 (a) shows the XRD patterns of ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup> (1–11 mol%) & (b) ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup> (5 mol%), pure SiO<sub>2</sub>, SiO<sub>2</sub>@ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup> (5 mol%) NP

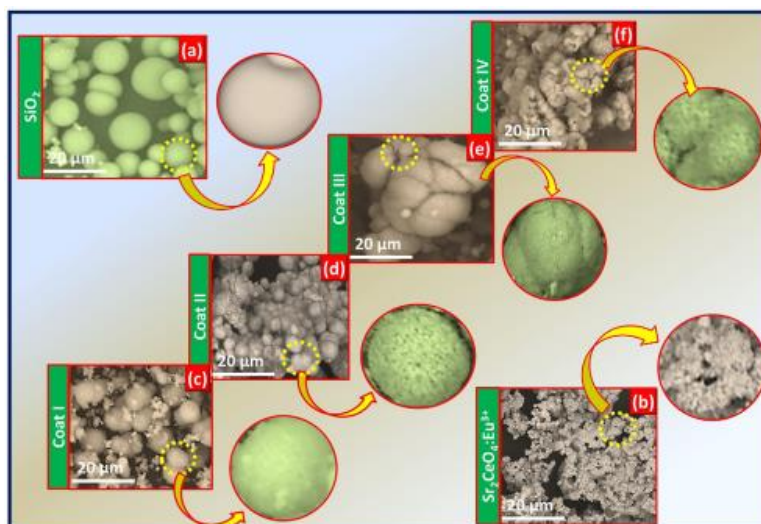
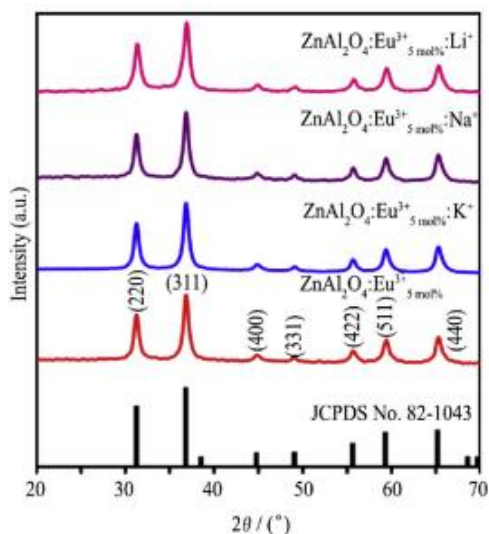


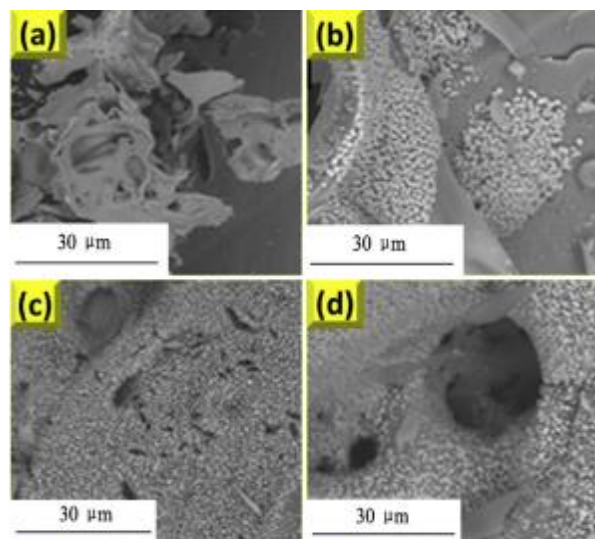
Fig.5.2. SEM micrographs of (a) SiO<sub>2</sub> core, (b) ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup> (5 mol%) NP and (c–f) core–shell SiO<sub>2</sub>@ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup> (5 mol%) NPs with (I–IV) coatings

### 4.3 Morphological study of ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup>, M<sup>+</sup> (M<sup>+</sup> = K<sup>+</sup>, Na<sup>+</sup> and Li<sup>+</sup>) nanoparticles

XRD patterns of ZnAl<sub>2</sub>O<sub>4</sub>:Eu<sup>3+</sup> (5 mol%) (ZAE) and ZAE: M<sup>+</sup> (M<sup>+</sup> = K<sup>+</sup>, Na<sup>+</sup> and Li<sup>+</sup>) (1 wt%) NPs are shown in Fig. 6.1. As can be seen from the figure, intense peaks at (220), (311), (400), (330), (422), (511) and (440) planes correspond to the cubic structure of ZnAl<sub>2</sub>O<sub>4</sub> and are consistent with JCPDS No. 82-1043. The surface morphologies of ZAE and ZAE: M<sup>+</sup> (M<sup>+</sup> = K<sup>+</sup>, Na<sup>+</sup> and Li<sup>+</sup>) NPs are shown in Fig. 6.2 (a - d). As can be seen from the micrographs, the product shows flaky, non-uniform in size which is an inherent nature of aluminates product. Upon co-doped with Na, Li and K ions in ZnAl<sub>2</sub>O<sub>4</sub>, smaller sized particles on the surfaces of the flakes are observed.



**Fig. 6.1.** PXRD patterns of ZAE:  $M^+$  ( $M^+ = K^+, Na^+$  and  $Li^+$ ) NPs



**Fig.6.2.** SEM images of (a) ZAE, (b) ZAE:  $K^+$ , (c) ZAE:  $Na^+$ , (d) ZAE:  $Li^+$

## CONCLUSIONS

A series of  $ZnAl_2O_4:Tb^{3+}$  (0.25–5 mol%) nanophosphors were synthesized by self-sacrificial A.V. gel assisted ultrasonication method. This method offered more advantages including fast and simple process with reproducibility of nanostructures and their possible applications. Various structural evolutions of present samples were systematically investigated by SEM studies.

Bi-functional (UV and white light illuminated) composite core-shell  $SiO_2@ZnAl_2O_4:Eu^{3+}$  nanoparticles were successfully synthesized and surface was modified via facile and cost effective solvothermal process. The  $SiO_2$  cores were smooth, non-agglomerated and spherical in nature with different sizes. After coating the  $SiO_2$  cores on  $ZnAl_2O_4:Eu^{3+}$  (5 mol%) NPs, the resultant nanoparticle was found to be agglomerated and marginally higher than the pure spherical particles.

Alkali metal ions ( $Li^+$ ,  $Na^+$ ,  $K^+$ ) doped ZAE powders were prepared via green combustion route using *Mimosa pudica* leaves extract as fuel. The micrographs showed flaky, non-uniform in size which is an inherent nature of aluminates product. Upon co-doped with Na, Li and K ions in  $ZnAl_2O_4$ , smaller sized particles on the surfaces of the flakes are observed.

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