

# Synthesis and Morphology Properties of Mn-doped Zinc Aluminate ( $\text{ZnAl}_{2-x}\text{O}_4: x\text{Mn}^{4+}$ , $x=1\%$ ) Using Co-Precipitation Methods with Microwave Thermal Assisted

B W Nuryadin<sup>1,2\*</sup>, Asti Sawitri<sup>1,2</sup>, E C S Mahen<sup>1,3</sup>, and A Y Nuryantini<sup>1,3</sup>

<sup>1</sup>Laboratorium Nanomaterial Fisika, Universitas Islam Negeri Sunan Gunung Djati  
Jalan A.H. Nasution 105, Cibiru – Bandung 40614, Indonesia

<sup>2</sup>Departemen Fisika, Universitas Islam Negeri Sunan Gunung Djati Bandung  
Jalan A.H. Nasution 105, Cibiru – Bandung 40614, Indonesia

<sup>3</sup>Departemen Pendidikan Fisika, Universitas Islam Negeri Sunan Gunung Djati  
Jalan A.H. Nasution 105, Cibiru – Bandung 40614, Indonesia

Email: bebehwahid102@uinsgd.ac.id

**Abstract.**  $\text{ZnAl}_2\text{O}_4: \text{Mn}^{4+}$  particle were synthesized using co-precipitation using NaOH and PVA as precipitating agent and surfactants, followed by microwave-assisted thermal treatment. The morphology properties and absorption spectral of particles were investigated using SEM and UV-Vis spectrometer. The results showed that the  $\text{ZnAl}_2\text{O}_4$  particles have a spinel structure with various particle sizes. Absorption spectra exhibit that the particle has potential photocatalytic properties at visible light spectra, especially for pollutant degradation.

## 1. Introduction

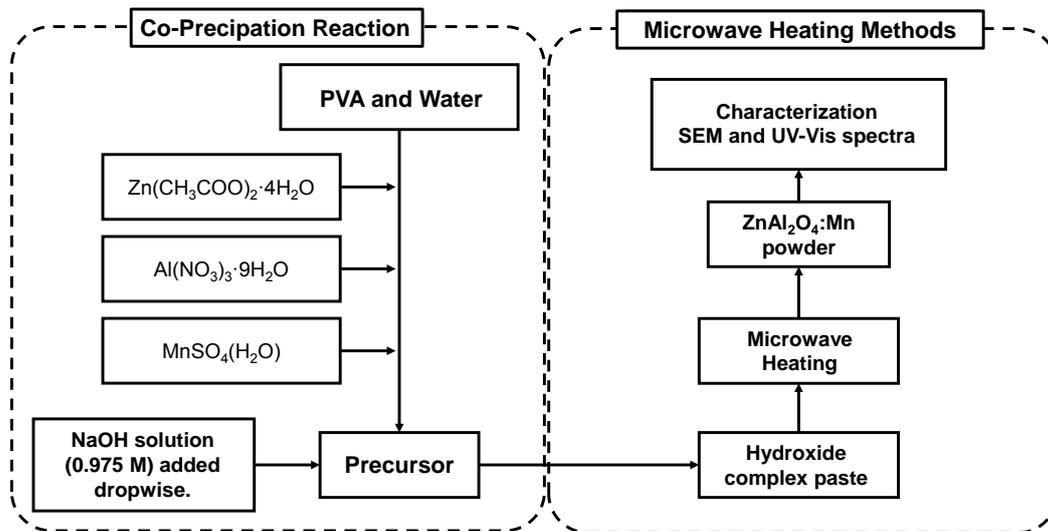
Zinc aluminate ( $\text{ZnAl}_2\text{O}_4$ ), related to the electronic structure  $Fd3m$  [1], is a semiconductor material with a wide energy band gap (3.8-3.9 eV).  $\text{ZnAl}_2\text{O}_4$  material has superior semiconductor properties, such as low surface acidity levels, high thermal stability, electronic and optical properties, and hydrophobic. Therefore, these materials could be developed as electroluminescence material, sensor, or a heterogeneous catalyst [2, 3].

In recent years, these various physical and chemical processes have been used to synthesize  $\text{ZnAl}_2\text{O}_4$ , such as sol-gel method [3], solid state reaction [4], hydrothermal [5], deposition [6] etc. Compared with other methods, the deposition method is faster, high levels of chemical homogeneity, easy in setting the composition and structure, and setting the particle size and morphology. However, this method requires a sintering process in order to produce the proper oxide particles.

In this paper,  $\text{ZnAl}_{2-x}\text{O}_4: x\text{Mn}^{4+}$  ( $x=1\%$ ) have successfully synthesized using the co-precipitation method.

Moreover, the process of microwave heating was used as part of the process of sintering material  $\text{ZnAl}_2\text{O}_4:\text{Mn}$ . Microscopic structure, morphology and optical properties of the sample of interest to be investigated and discussed closely.





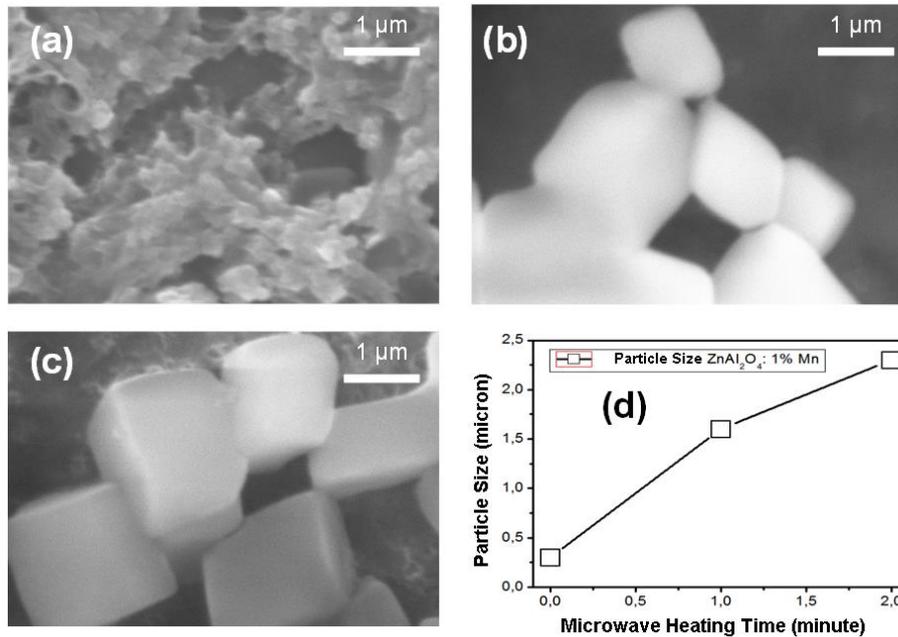
**Figure 1.** Synthesis scheme of ZnAl<sub>2</sub>O<sub>4</sub>:Mn particle using co-precipitation methods with microwave thermal assisted.

## 2. Experiment

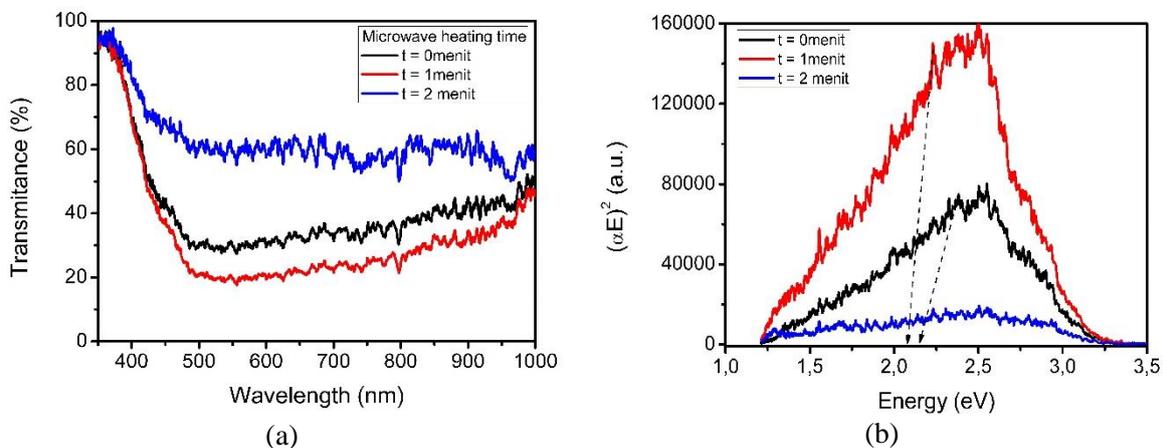
Manganese doped Zinc Aluminate (ZnAl<sub>2</sub>O<sub>4</sub>:Mn) synthesized using 0.5 g zinc acetate tetrahydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, BM= g/mol), 1.708 g aluminum nitrate nonahidrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, BM= g/mol) dan 0.0025 g mangan sulfat hidrate (MnSO<sub>4</sub>(H<sub>2</sub>O), BM= g/mol) as zinc, aluminum and mangan source, respectively. All of these chemicals will produce a material with the following composition ZnAl<sub>1.99</sub>O<sub>4</sub>: 1% Mn<sup>4+</sup>. First, 0.01 g of PVA (polyvinyl alcohol, BM = g / mol) as a surfactant dissolved in 100 ml of pure water. After that, all basic materials are dissolve to obtain a clear precursor solution. Then, a solution of NaOH (0.78 g NaOH in 20 ml of water solvent) is slowly dripped into a precursor solution (drop wise). From this process, coloured solution became white and a precipitate formed. Subsequently, the precipitate is separated from the solvent water using filter paper until obtain white paste. The white paste is a complex particles hydroxide (Zn(OH)<sub>2</sub>, Al(OH)<sub>3</sub>, and Mn(OH)<sub>2</sub>). To determine the effect of microwave heating on particle morphology ZnAl<sub>2</sub>O<sub>4</sub>:Mn, 1g complex hydroxide paste sample were heated using the microwave (800 watts) for 0 - 2 minutes, until white ceramic powder produced. The morphology and absorbance spectra of ZnAl<sub>2</sub>O<sub>4</sub>:Mn particle characterized using Scanning Electron Microscope (JEOL JCM-6000 NeoScope Benchtop SEM, Japan) and UV-Visible Spectroscopy (Home-Made Spectroscopy from LD-Didactic).

## 3. Results and Discussion

Figure 2 is a SEM image of the sample ZnAl<sub>2</sub>O<sub>4</sub>: Mn for some time variations microwave heating. Results precipitation reaction in the form of a white paste that we call complex hydroxide particles has a size in the range of 400 nm. Figure 2 (a). SEM observation showed that the hydroxide particles covered by the polymer layer of PVA. These causes the particles are not mutually agglomeration, and produce a particle size that is small enough. Microwave heating causes the particles undergo localized heating process. This is due to the microwave energy is absorbed by the particle turns into heat which is sufficient for the oxidation processes. Therefore, microwave heating transform complex particles into particles ZnAl<sub>2</sub>O<sub>4</sub>: Mn. In addition, the length of time the heating causes agglomeration caused by high heat and energy loss due to the polymer layer decomposes during microwave heating process, see Figure 2 (b) and 2 (c). It is characterize by an increase in particle size ZnAl<sub>2</sub>O<sub>4</sub>:Mn as the length of time the microwave heating, from 1.6 μm to 2.3 μm (Figure 2 (d)). This observation indicates that microwave heating is very effective in the process of sintering and particle oxidation.



**Figure 2.** SEM image of  $\text{ZnAl}_2\text{O}_4:\text{Mn}$  particle for various of microwave heating time, (a). 0 min, (b). 1 min, and (c) 2 min. While, (d). relation of  $\text{ZnAl}_2\text{O}_4:\text{Mn}$  particle size distribution with heating time.



**Figure 3.** (a) Absorbance spectra, and (b) Tauc plot analysis of  $\text{ZnAl}_2\text{O}_4:\text{Mn}$  particle with various of heating time, all sample prepared with 0,01 g of  $\text{ZnAl}_2\text{O}_4:\text{Mn}$  particle at 5 ml of pure water.

Figure 3 is an absorbance spectrum of particle observations  $\text{ZnAl}_2\text{O}_4:\text{Mn}$  in the synthesized at some time variations synthesis. The results of these observations have managed to show that the sample absorbance spectrum of wide area, hingg 900 nm to 500 nm, with a peak at around 650 nm. Observations showed differences absorbance spectrum intensity for each sample time microwave heating. This probably caused by the quality of crystallization and particle size  $\text{ZnAl}_2\text{O}_4:\text{Mn}$ . The intensity of the absorbance spectrum in the wavelength range of blue-yellow (400-500 nm) is very low. This probably caused by the emission properties (luminescence) particle  $\text{ZnAl}_2\text{O}_4:\text{Mn}$ , this part needs to be studied further.

The optical band gap calculated using the Tauc plots relationship. Expressed by,

$$(\alpha hv) = C(hv - E_g)^n \quad (1)$$

where  $C$  is a constant,  $\alpha$  is absorbance coefficient,  $E_g$  is the optical band gap of material, and  $n$  depends on the type of transition ( $n = 2$  or  $1/2$  for direct band gap and indirect band gap) [????]. The calculated optical band gap of ZnAl<sub>2</sub>O<sub>4</sub>:Mn particle from Tauc plots was found to be 2.7 eV as shown in Fig. 3(b). The calculation results showed that all samples have the similar value of optical band gap.

#### 4. Conclusions

Particle ZnAl<sub>2</sub>O<sub>4</sub>: Mn was synthesized using microwave heating assisted deposition. Observations show that the particle morphology occurs localized heating process that causes agglomeration or formation of large particles. Moreover, observations with absorbance, particle ZnAl<sub>2</sub>O<sub>4</sub>: Mn is estimate to have photocatalytic properties. Thus the particles ZnAl<sub>2</sub>O<sub>4</sub>: Mn has the potential to be develop as a photocatalytic material especially for liquid waste degradation.

#### 5. References

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