

# Synthesis and Characterization of ZnAl<sub>2</sub>O<sub>4</sub> Nanopowders by a Reverse Micelle Processing

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**Abstract** Using reverse micelle processing, ZnAl<sub>2</sub>O<sub>4</sub> nanopowders were synthesized from a mixed precursor (consisting of Zn(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub>). The ZnAl<sub>2</sub>O<sub>4</sub> was prepared by mixing the aqueous solution at a molar ratio of Zn : Al = 1 : 2. The average size and distribution of the synthesized powders with heat treatment at 600 °C for 2 h were in the range of 10-20 nm and narrow, respectively. The average size of the synthesized powders increased with increasing water to surfactant molar ratio. The XRD diffraction patterns show that the phase of ZnAl<sub>2</sub>O<sub>4</sub> was spinel (JCPDS No. 05-0669). The synthesized and calcined powders were characterized using a thermogravimetric - differential scanning calorimeter (TG-DSC), X-ray diffraction analysis (XRD), and high resolution transmission electron microscopy (HRTEM). The effects of the synthesis parameter, such as the molar ratio of water to surfactant, are discussed.

**Key words** ZnAl<sub>2</sub>O<sub>4</sub>, nanopowders, reverse micelle processing.

## 1. Introduction

The synthesis of nano-crystalline spinel has been investigated intensively because of the unique potential applications of nano-crystalline spinels in high density magnetic recording and microwave devices, magnetic fluids, and also as an absorbent material to remove sulfide gases from hot-coal gas.<sup>1-2)</sup> The spinels are complex oxides and represented by the general formula of A<sup>2+</sup>B<sup>3+</sup>O<sub>4</sub>. Zinc aluminate spinel (ZnAl<sub>2</sub>O<sub>4</sub>) has been widely used as catalyst, optical coating or host matrix, ceramics and electro-conductive materials because of its high thermal stability, high mechanical resistance, low surface acidity, and excellent optical properties.<sup>3-11)</sup>

In general, there are many methods of preparation of zinc aluminate, for example, solid state-reaction or wet chemical routes such as co-precipitation, sol-gel and hydrothermal method.<sup>12-17)</sup> Compared to other method, the reverse micelle method is one of the most promising wet chemistry syntheses. This method provides a favorable microenvironment for controlling the chemical reaction. So we could easily control the reaction rate in this

method, compared to other method, and we were able to obtain a narrow size distribution of nanoparticles.<sup>18)</sup> Reverse micelle solutions are transparent, isotropic, thermodynamically stable water-in-oil microemulsion in which the aqueous phase is dispersed as nanosized droplets surrounded by a monolayer of molecules in the continuous a polar organic phase.<sup>19-20)</sup> The surfactant-stabilized water pools provide a microenvironment for the preparation of ultrafine particles by exchanging their contents via the fusion-redispersion process and by preventing the excess aggregation of particles.<sup>21-22)</sup> Therefore, the particles obtained in such a medium are very fine and mono-dispersed.

The objective of this study is to prepare the nanosized ZnAl<sub>2</sub>O<sub>4</sub> powders with paramagnetic property by reverse micelle method and to investigate the effects of the processing conditions on the formation, morphology and phase of the powders.

## 2. Experiment

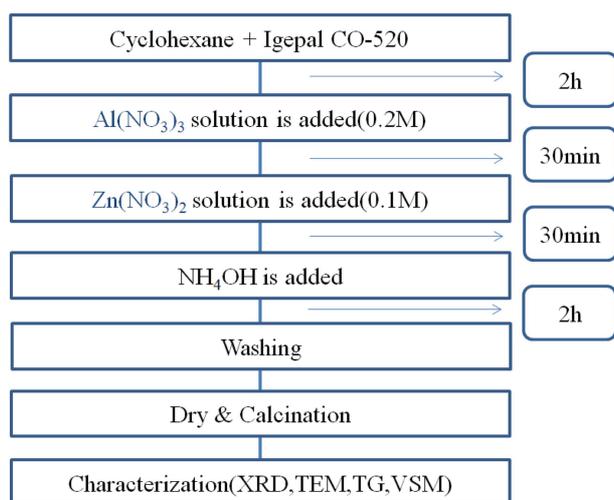
Fig. 1 shows the schematic illustration of the reverse

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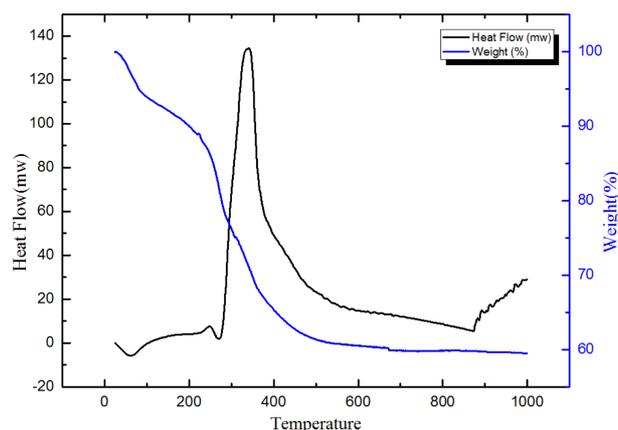
**Fig. 1.** Experimental flow chart of synthesized ZnAl<sub>2</sub>O<sub>4</sub> powders by reverse micelle processing.

micelle method. Al(NO<sub>3</sub>)<sub>3</sub> and Zn(NO<sub>3</sub>)<sub>2</sub> were used as the precursors of aluminum oxide and zinc, respectively. An aqueous solution of the precursors was prepared by dissolving Zn(NO<sub>3</sub>)<sub>2</sub> (0.1 M) and Al(NO<sub>3</sub>)<sub>3</sub> (0.2 M) in distilled water to a molar ratio of 1:2. Cyclohexane (Sigma Aldrich) was used as the solvent. Reverse microemulsion was prepared by mixing 40 mL of nonionic surfactant (poly(oxyethylene) nonylphenyl ether, Igepal CO-520, Aldrich, USA), 100 ml of cyclohexane and 6.5-13 ml of mixed aqueous solution (Zn : Al = 1 : 2). The microemulsion was stirred vigorously, and after 5 min of equilibration, 5-10 ml of NH<sub>4</sub>OH (28 %, Dae Jung Chemicals, Korea) was injected into the microemulsion. The particles were subsequently washed using ethanol to remove any residual surfactant. The dried powders were then heat-treated in air at the temperature range of 600-1100 °C.

The thermal characteristics of the powders were determined by thermogravimetry (TG) and differential scanning calorimetry (DSC) techniques (SCINCO, STA 1500, Korea). The recovered powders were analyzed for phase composition using X-ray diffraction (XRD, Philips X'pert MPD PW3040, Holland) over the 2θ range from 20° to 80° at the scan speed of 2° min<sup>-1</sup>. The morphology of the synthesized particles was observed using transmission electron microscope (TEM, Jeol 2000FXII, Japan). For TEM studies, samples were prepared by adding drops of freshly prepared cluster solution on a carbon film supported on a Cu grid. The magnetic property of the powder was measured by Vibrating Sample Magnetometer (VSM, Lake shore, USA) at 298K.

### 3. Results and Discussion

Ternary systems of Cyclohexane/Igepal CO 520/water

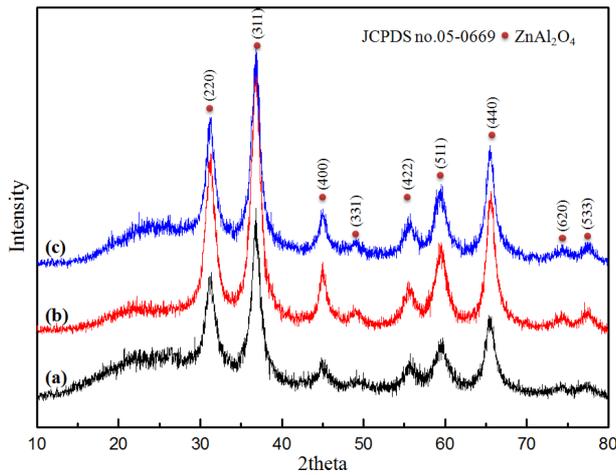


**Fig. 2.** TG-DSC curves of ZnAl<sub>2</sub>O<sub>4</sub> nanoparticles at R = 8 by reverse micelle process (temperature : 1000 °C, holding time: 10 min).

offer certain advantages: they are spheroidal and mono-disperse aggregates where water is readily solubilized in the polar core, forming a 'water pool' characterized by the ratio of water to surfactant concentration. Another important property of reverse micelles is their dynamics character; the water pools can exchange their contents by a collision process. The aggregation and self-assembly of the oil/surfactant/water species is complex, and very little is known about the cluster growth and final nanostructure as a function of synthesis conditions. The molar ratio of water to surfactant can determine the size of the microemulsion water core.<sup>23)</sup> Therefore, the diameter of the nanoparticles in the microemulsion can be controlled by the water/surfactants molar ratio (R) and Zn molar ratio (x = 0.4) at aqueous solution value. In this present study we have chosen x = 0.4 because magnetic moment decreased as the concentration of increased to x = 0.5 due to lattice perfection which is caused by increased number of Zn ions on the A site, as result of according as interaction increases with spin of B site by magnetic moment of A site is weak, magnetic moment is decreased that semi-balance ingredient is grown.<sup>24)</sup>

Fig. 2 shows the typical thermal behavior of the ZnAl<sub>2</sub>O<sub>4</sub> nanoparticles. The TG curve shows a total weight loss of 40 % at 800 °C. The endothermic peak at 60 °C observed in DSC curve is attributed to the evaporation of the absorbed water and the dehydration, accompanied by significant weight loss. The two exothermic peaks at 250 °C and 340 °C are the burning of organics and correspond to the crystallization of the ZnAl<sub>2</sub>O<sub>4</sub> spinel.

Fig. 3 shows the X-ray diffraction pattern of the ZnAl<sub>2</sub>O<sub>4</sub> nanoparticles with calcination at 800 °C for 2h as a function of R value (water/surfactants molar ratio). With the R value from 4 to 8, the intensity of the diffraction peaks increases, this is associated with an increase of crystallinity. The crystallinity of synthesized ZnAl<sub>2</sub>O<sub>4</sub>



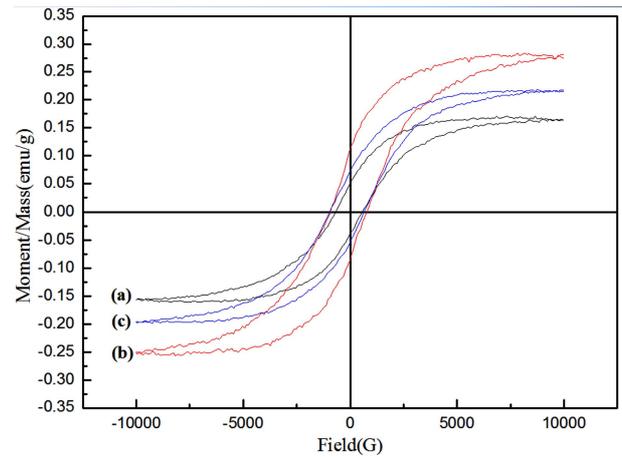
**Fig. 3.** XRD patterns of  $\text{ZnAl}_2\text{O}_4$  powders calcined at  $800\text{ }^\circ\text{C}$  for 2h as a function of R value (water /surfactants molar ratio): (a)  $R = 4$ , (b)  $R = 6$  and (c)  $R = 8$ .

nanoparticles was the highest at 6 of R value. All peak indexed as (220), (311), (400), (511) and (440) in XRD patterns were assigned to Cubic  $\text{ZnAl}_2\text{O}_4$  spinel structure (JCPDS Card No. 05-0669).  $\text{ZnAl}_2\text{O}_4$  is the only phase detected in all the calcined samples.

Fig. 4 shows the transmission electron microscopy (TEM) of the synthesized  $\text{ZnAl}_2\text{O}_4$  particles with calcination at  $800\text{ }^\circ\text{C}$  for 2h as a function of water/surfactants molar ratio.

The average sizes of the synthesized  $\text{ZnAl}_2\text{O}_4$  nanoparticles are no changed with the R value increased from 4 to 8. The morphology and particle size distribution of the synthesized  $\text{ZnAl}_2\text{O}_4$  nanoparticles are nearly spherical and broad, respectively. The particle sizes are about 5–10 nm. The SAED patterns indicate the prepared  $\text{ZnAl}_2\text{O}_4$  nanoparticles were crystalline. The nucleation and growth are controlled by interaction between micelles, phase behavior and solubility, average occupancy of the reacting species in the aqueous medium, dynamic behavior of the reverse micellar solution and so on.<sup>25)</sup>

Fig. 5 show magnetic properties of the  $\text{ZnAl}_2\text{O}_4$  powders at  $R = 8$  after different calcination temperature. From the VSM analysis, the synthesized nanosized crystalline powder exhibiting paramagnetic property. The coercive force



**Fig. 5.** Magnetic properties of  $\text{ZnAl}_2\text{O}_4$  powders prepared at  $R = 8$  after calcination: (a)  $600\text{ }^\circ\text{C}$ , (b)  $800\text{ }^\circ\text{C}$ , and (c)  $1100\text{ }^\circ\text{C}$  for 2h.

**Table 1.** Magnetic properties of  $\text{ZnAl}_2\text{O}_4$  at  $R = 8$  after different calcination temperature.

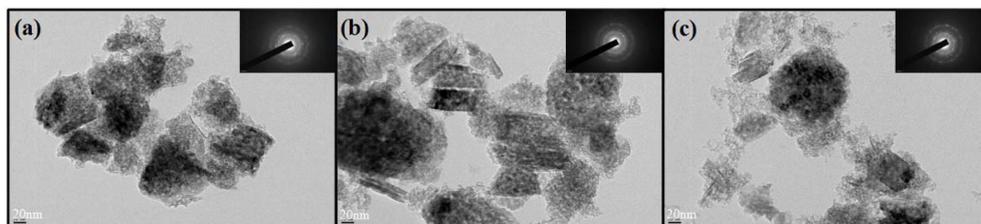
Calcination Temperature	Coercivity	Saturation Magnetization	Residual Magnetizations
$600\text{ }^\circ\text{C}$	619.38	0.17097	44.851E-3
$800\text{ }^\circ\text{C}$	849.11	0.28373	98.309E-3
$1100\text{ }^\circ\text{C}$	801.82	0.21899	63.486E-3

showed a maximum value at  $800\text{ }^\circ\text{C}$ .

The deduced value of saturation magnetization is given in Table 1. The saturation magnetization values of samples are 0.17097, 0.28373 and 0.21899 emu/g, when the powders are calcined at  $600\text{ }^\circ\text{C}$ ,  $800\text{ }^\circ\text{C}$  and  $1100\text{ }^\circ\text{C}$ , respectively.

#### 4. Conclusions

$\text{ZnAl}_2\text{O}_4$  nanoparticles have been prepared using a reverse micelle process. X-ray diffraction pattern of the synthesized particles observed diffraction peaks correspond to the standard patterns of  $\text{ZnAl}_2\text{O}_4$  spinel structure. The water/surfactant molar ratio (R value) influenced the average size and distribution of the synthesized particles. The average sizes of the synthesized  $\text{ZnAl}_2\text{O}_4$  powder were about 5–10 nm. Reverse micelle synthesis of



**Fig. 4.** TEM images (inset SAED patterns) of  $\text{ZnAl}_2\text{O}_4$  powders with calcination at  $800\text{ }^\circ\text{C}$  for 2h prepared by a reverse micelle process: (a)  $R = 4$ , (b)  $R = 6$  and (c)  $R = 8$ .

ZnAl<sub>2</sub>O<sub>4</sub> powders yielded a nano-sized crystalline powder exhibiting paramagnetic character. If the water/ surfactant molar ratio and mixture ratio of the aqueous solutions is carefully controlled, it is possible to control the average size, crystalline phase and magnetic property of the synthesized powders.

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