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Effect of Cu$^{2+}$ ions on structural, morphological, optical and magnetic behaviors of ZnAl$_2$O$_4$ spinel

T Sofia Nirmala 1, N Iyandurai 2, S Yuvaraj 3 and M Sundararajan 4

1 Department of Physics, Loyola College of Arts and Science, Mettala, Namakkal 636 202, Tamil Nadu, India
2 PG and Research Department of Physics, Thiruvalluvar Government Arts College, Rasiapuram, Namakkal 636 401, Tamil Nadu, India
3 Department of Physics, Karpagam Academy of Higher Education, Coimbatore 641 021, Tamil Nadu, India
4 PG and Research Department of Physics, Paavendhar College of Arts & Science, M.V. South, Attur, Salem 636 121, Tamil Nadu, India

E-mail: iyandurain86@gmail.com

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Abstract

Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ nanoparticles were prepared by microwave combustion technique with metal nitrates as precursor materials. Powder x-ray diffraction studies confirm the formation of single phase of spinel pure and copper doped zinc alumimates. HR-SEM images reveal the agglomerated coalescence morphology with pores. Elemental analysis (EDX) confirm the presence of Zn, Cu, Fe and O. UV-Visible Diffuse reflectance spectroscopy is used to find the optical bandgap and it is found to decreases from 5.45 eV to 3.57 eV. IR spectra show three major peaks which confirm the phase formation of Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ nano aluminates with spinel structure. Vibrating sample magnetometer (VSM) measurements reveal the super paramagnetic nature of pure and copper doped zinc alumimates. The obtain results are confirmed that present pure and copper doped ZnAl$_2$O$_4$ particles at nanoscale are to be potential candidate for catalytic, sensor and optoelectronic device applications.

1. Introduction

The extraordinary growth in nanotechnology has been achieved by applying the materials at nanoscale. The various properties like biological [1], catalytic [2], magnetic [3], electrical [4] and optical behavior can be modified when the bulk materials transform into nanomaterials with similar chemical composition [5]. From several inorganic solids, mixed metallic oxides with spinel structure are very familiar for their unusual and unique properties. Spinel structured metal oxides are highly stable materials with large resistance, very cheap and non-toxic [6]. In general, spinel-kind metallic oxide have the chemical formula AB$_2$O$_4$, where A denotes divalent metal ions (Cu$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, etc.), B denotes trivalent metal ions (Fe$^{3+}$, Cr$^{3+}$, Al$^{3+}$, etc.), and occupies the center of tetrahedral and octahedral sites respectively. They are mostly applied in sensor and semiconductor industry owing to their structural characteristics [7]. In the past few decades, many researchers have proven the application of these spinel structured materials in the evolution of technological devices due to their outstanding physical and chemical behavior [8, 9]. In particular, aluminate spinel possess low surface acidity, hydrophobicity, high mechanical resistance and high thermal stability [10, 11]. These peculiar behaviors make them as prominent material in various applications to change the current technology [12].

Among spinel metal alumimates, zinc aluminate nanomaterial is very known semiconductor with large energy gap (3.5 to 3.9 eV) [13]. Rare mineral ZnAl$_2$O$_4$ which have normal spinel structure exhibit excellent optical, electrical and magnetic behavior [14, 15]. Zinc aluminate used as catalysts [16], high temperature materials [17] and optical materials [18, 19].

Copper aluminate with cubic spinel structure is a remarkable candidate in photocatalysts application due to their high magnetic behavior [7]. Magnetic, optical, electrical and structural characteristics of host materials can be improved by doping of copper ions which lead to alter the chemical composition of host material. Even though zinc atoms are non-magnetic, addition of copper ions modify the whole structure of host material (from normal spinel to inverse spinel) and improve the magnetic characteristics [19]. Especially copper doped metal
aluminates utilized in different applications like gas-sensor, massive storage and spintronic device. In particular, Zn–Cu spinel aluminates exhibit supreme magnetic properties depend on the percentage of Cu$^{2+}$ ions in zinc aluminate. Great resistivity, higher initial permeability and large magnetic saturation of Zn–Cu aluminates make them as better candidate for several applications such as inductors, electrical switch, microwave latching device, transformers, antenna cores and memory devices, etc [20–22]. Generally zinc aluminates spinel were synthesized by different ways like hydrothermal [14, 23], sol-gel, co-precipitation route [24], solid-state reaction [25, 26] and microwave combustion [27]. Among various synthesis route, microwave combustion technique is an easy and attractive method for synthesis of zinc aluminate at nanoscale due to high yield of ultrafine and pure powders. It is noted that citric acid, propylene glycol and urea are widely employed as fuels to synthesize zinc aluminates using microwave combustion technique.

In this paper, Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ (x = 0.0, 0.1, 0.3 and 0.5) nanoparticles are prepared by employing microwave combustion method utilizing L-arginine as fuel. Structural, morphological, optical and magnetic characteristics of the obtained Cu/ZnAl$_2$O$_4$ nanoparticles are analyzed using methods such as powder x-ray diffraction (XRD), high resolution scanning electron microscopy (HR-SEM), energy dispersive x-ray spectroscopy (EDX), UV-Visible diffuse reflectance spectroscopy (UV-DRS), Fourier transform infrared spectroscopy (FTIR) and vibrating sample magnetometer (VSM).

2. Experimental

2.1. Synthesis

In order to synthesize Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ nanoparticles zinc nitrate (Zn(NO$_3$)$_2$ · 6H$_2$O, 98%), copper nitrate (Cu(NO$_3$)$_2$ · 3H$_2$O, 98%), aluminum nitrate (Al(NO$_3$)$_3$ · 9H$_2$O, 98%) are used as precursor material and L-alanine (C$_3$H$_7$NO$_2$, 99%) as fuel. The chemicals used for performing experiments are of analytical grade got from SD fine, India and utilized as it is without performing additional purification. Double deionized water is employed for the preparation of the samples.

The precursors like zinc, copper and aluminum nitrate were prepared in the mole ratio of 1:2 to attain homogeneous solution and were added to aluminum nitrate and L-alanine solution. This blended solution is kept under one hour constant stirred. The nitrates act like an oxidizer while L-alanine used as fuel. Following the norm of propellant chemistry the ratio of fuel to oxidizer (F/O) is maintained to be one. The resultant solution is dispensed into a silica crucible and placed in domestic microwave oven (SAMSUNG, India Limited) for the process of irradiation.

Initially, output power is set in the microwave oven for 15 min at 700 Watts and frequency of 2.54 GHz. When the microwave energy is given the solution went through the sequence of process such as boiling, vaporizing, dehydration followed by decomposition which results in reaction gas evolution. As spontaneous combustion of solution occurred, further ignition takes place under the influence of rapid flame causing the fluffy production of Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ (0 ≤ x ≤ 0.5) nanoparticles. Hence, the obtained sample washed with distilled water, ethanol and dried at 90 °C for 1 h. The final obtained products such as ZnAl$_2$O$_4$, Zn$_{0.9}$Cu$_{0.1}$Al$_2$O$_4$, Zn$_{0.7}$Cu$_{0.3}$Al$_2$O$_4$ and Zn$_{0.5}$Cu$_{0.5}$Al$_2$O$_4$ it labelled as ZA1, ZCuA2, ZCuA3 and ZCuA4 respectively.

The chemical reactions that influence the process of formation of pure and copper doped zinc aluminate nanoparticles during the microwave combustion process using L-alanine is as follows:

\[
\text{Zn(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O(S)} + 2\text{Al(NO}_3\text{)}_3\cdot 3\text{H}_2\text{O(S)} + 2\text{C}_3\text{H}_7\text{NO}_2\text{2(1S)} \rightarrow \text{ZnAl}_2\text{O}_4\text{(S)} + 5\text{N}_2(\uparrow) + 8\text{CO}_2(\uparrow) + 33\text{H}_2\text{O}(\uparrow) \quad (1)
\]

2.2. Characterization

Crystalline structure and phase analysis of pure and copper doped zinc aluminate nanoparticles were obtained within the range of 20° to 80° using powder x-ray diffractometer with CuKα radiation at λ = 1.5406 Å (Model RigakuUltima III). The morphology and elemental study is performed through using an energy dispersive x-ray analyser equipped with FEI Quanta FEG 200 scanning electron microscope. Optical band gaps were calculated by using diffuse reflectance spectrum was (DRS-UV visible Spectrometer) recorded by utilizing the double beam Perkin Elmer (Thermo Scientific Evolution 220) spectrophotometer within 200–800 nm. The FTIR spectra recorded on a Perkin Elmer spectrophotometer (Spectrum RXI). Vibration sample magnetometry was recorded at room temperature utilizing (Lake Shore, USA, Model 7404 with 3 magnets).
3. Results and discussion

3.1. Structural analysis

Powder x-ray diffraction study is utilized to identify the phase formation of synthesized nano aluminates. Figure 1 exhibits the powder x-ray diffraction pattern of Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ $(0 \leq x \leq 0.5)$ nanoparticles. It demonstrates that obtained pattern have nine diffracted peaks at 31.2°, 36.75°, 44.7°, 49.1°, 55.6°, 59.3°, 65.3°, 74.1° and 77.3° and matched with (220), (311), (400), (331), (422), (511), (440), (620) and (533) hkl planes respectively. These hkl planes are clearly match with standard JCPDS card no 82-1043 which confirm the phase formation of cubic spinel zinc aluminite nanoparticles with Fd$ar{3}$m space group [28]. The absence of extra peaks confirm non-appearance of secondary impure phase. As shown in figure 1, addition of copper ions into ZnAl$_2$O$_4$ nano aluminates indicated by peak shift from higher diffracting angle to lower diffracting angle. The lattice parameters are estimated and shown in table 1 for Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ $(0 \leq x \leq 0.5)$ nanoparticles. The value of lattice parameters decreases from 8.140 Å to 8.100 Å as increases Cu$^{2+}$ ion concentrations in zinc aluminates. It is due to lower ionic radii of copper $(0.57$ Å$)$ compare to zinc ionic radii $(0.60$ Å$)$. Debye-Scherrer formula is used to estimate the mean crystallite size. It is identified that the estimated crystallize size values are 11.40 nm, 13.10 nm, 14.15 nm and 17.01 nm for $x = 0, 0.1, 0.3$ and 0.5 respectively. Linear increase of crystallite size is assigned to the formation of higher nanoclusters which is shown in SEM image.

From Williamson-Hall plot Lattice strain and effective crystallite size are deduced. These structural parameters are estimated through the formula [31]

$$\frac{\beta \cos \theta}{\lambda} = \frac{k}{D} + \frac{4\varepsilon \sin \theta}{\lambda}$$

(2)

Where, $\beta$ is full width half maximum, $\lambda$ is the source wavelength, $\theta$ is the diffracted angle, $k$ is the constant, $\varepsilon$ is the permittivity of free space and $D$ is the effective crystallite size. The graph is plotted between $4\sin \theta/\lambda$ and $\beta \cos \theta/\lambda$. Effective crystallite sizes attain from the intercept $(k/D)$ on $y$-axis and lattice strain attain from slope of the plot. As shown in figure 2, the slope line is changing from positive to negative terminal for Zn$_{2-x}$Cu$_x$Al$_2$O$_4$ system. It is owing to the lower ionic radii of copper ion induce lattice contraction and reflected in linear decrease of lattice strain values as increase of Cu$^{2+}$ ion into ZnAl$_2$O$_4$ system. The effective crystallite size are found to be

![Figure 1. Powder x-ray diffraction pattern of Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ $(0 \leq x \leq 0.5)$ nanoparticles.](image)

Table 1. Crystallite size, lattice parameter and energy gap of Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ $(0 \leq x \leq 0.5)$ nanoparticles.

| Sample name         | Crystallite size, L (nm) | Effective crystallite size, D (nm) by William-hall plot | Lattice parameter, $a$ (Å) | Energy gap (eV) | Strain, $\varepsilon$ |
|---------------------|--------------------------|--------------------------------------------------------|-----------------------------|-----------------|-----------------------|
| ZnAl$_2$O$_4$        | 11.40                    | 12.10                                                  | 8.140                       | 5.45            | 0.061 08              |
| Zn$_{0.9}$Cu$_{0.1}$Al$_2$O$_4$ | 13.10                  | 13.55                                                  | 8.130                       | 4.26            | 0.049 12              |
| Zn$_{0.7}$Cu$_{0.3}$Al$_2$O$_4$ | 14.15                  | 15.35                                                  | 8.121                       | 3.96            | 0.040 18              |
| Zn$_{0.5}$Cu$_{0.5}$Al$_2$O$_4$ | 17.01                  | 18.04                                                  | 8.100                       | 3.57            | 0.001 68              |

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The lattice parameters are estimated [29] and shown in table 1 for Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ $(0 \leq x \leq 0.5)$ nano aluminates. The value of lattice parameters decreases from 8.140 Å to 8.100 Å as increases Cu$^{2+}$ ion concentrations in zinc aluminates. It is due to lower ionic radii of copper $(0.57$ Å$)$ compare to zinc ionic radii $(0.60$ Å$)$. Debye-Scherrer formula [30] is used to estimate the mean crystallite size. It is identified that the estimated crystallize size values are 11.40 nm, 13.10 nm, 14.15 nm and 17.01 nm for $x = 0, 0.1, 0.3$ and 0.5 respectively. Linear increase of crystallite size is assigned to the formation of higher nanoclusters which is shown in SEM image.

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12.10 nm, 13.55 nm, 15.35 nm and 18.04 nm for $x = 0, 0.1, 0.3$ and 0.5 respectively. Small variation between the size of effective crystallite size and average crystallite size (Debye-Scherrer) is owing to internal strain take into consideration in W-H plot.

3.2. High resolution scanning electron microscopy analysis
High resolution scanning electron microscopy study is used to get details about shape and surface morphology of pure and copper doped zinc nano aluminates. As shown in figure 3, it is noticed that trend of agglomerated...
coalescence morphology with large number of pores. In this case, the existence of a large number of gas molecules at the time of combustion process causes the different sizes of pore in the surface of pure and copper doped zinc aluminates system. Moreover, it is found that the particle dimension is in the range of 10–17 nm which is very close to powder XRD data.

3.3. Energy dispersive x-ray spectroscopy analysis

The quantitative and elemental analyses are done with energy dispersive x-ray spectroscopy. Figure 4 shows the EDX spectra of Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ nanoparticles. EDX spectra reveal the presence of Zn$^{2+}$, Cu$^{2+}$, Al$^{3+}$ and O$^{2-}$ elements. The absence of extra impure elements confirm the purity of starting precursors. It is seen that the molar of Zn/Cu:Al is nearly close to stoichiometric ratio of 1:2.

3.4. Diffuse reflectance spectroscopy analysis

UV-visible diffuse reflectance spectroscopy is utilized to study the optical characteristics of pure and copper doped zinc nano aluminates. Kubelka-Munk function [32] is used to change the reflectance data into linear absorption coefficient.

$$\alpha = F(R) = \frac{(1 - R)^2}{2R}$$  \hspace{1cm} (3)

Where, $F(R)$ is Kubelka-Munk function and $R$ is reflectance data. Tauc relation [33] is utilized to determine the optical bandgap,

$$\alpha \nu = A(\nu - E_g)^n$$  \hspace{1cm} (4)

Where $A$ is the constant (edge width parameter), $E_g$ is the optical band gap, $\alpha$ is the linear absorption coefficient, $n$ is the optical transition (n = 1/2 indicates indirect energy bandgap and n = 2 indicates direct energy bandgap). $(\alpha \nu)^2$ versus $\nu$ graph shown in figure 5 for Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ (0 ≤ x ≤ 0.5) nanoparticles. In this case, linear extrapolation has chosen for n = 2 to find the direct optical bandgap of synthesized pure and copper doped zinc aluminates. It is found that the optical bandgap values are 5.45 eV, 4.26 eV, 3.96 eV and 3.57 eV for

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**Figure 4.** EDX spectra of (a) ZnAl$_2$O$_4$ (b) Zn$_{0.9}$Cu$_{0.1}$Al$_2$O$_4$ (c) Zn$_{0.7}$Cu$_{0.3}$Al$_2$O$_4$ and (d) Zn$_{0.5}$Cu$_{0.5}$Al$_2$O$_4$ nanoparticles.
x = 0, 0.1, 0.3 and 0.5 respectively. Moreover, impurities, carrier concentration and lattice concentration may influence the optical bandgap of the materials. Here, decrease in optical bandgap values as increases Cu²⁺ ion concentration suggest the insertion of new energy levels between the band structures [34].

3.5. Fourier transforms infrared spectroscopy analysis

Fourier transform infrared spectroscopy analysis is used to know about the functional group presents in the sample. Some parameters like unit cell, cation mass, cation-oxygen bonding force, cation distance and distributions may affect the vibrational frequencies of nano aluminates. Figure 6 reveals the FTIR spectra of Zn₁₋ₓCuₓAl₂O₄ nanoparticles between the mid IR of 400–4000 cm⁻¹. The vibrational peaks is observed at 501 cm⁻¹, 577 cm⁻¹, 670 cm⁻¹, 1639 cm⁻¹, 2929 cm⁻¹, 2845 cm⁻¹ and 3480 cm⁻¹. The first three peaks at 501 cm⁻¹, 577 cm⁻¹ and 670 cm⁻¹ confirm the phase formation of spinel zinc aluminates [35]. The peak at 501 cm⁻¹ is corresponding to metal (Al³⁺–O²⁻) stretching vibrations at octahedral site where other two peaks 577 cm⁻¹ and 670 cm⁻¹ is assigned to metal (Zn/Cu²⁺–O²⁻) stretching vibration at tetrahedral site [36]. As shown in FTIR spectra, incorporation of Cu²⁺ ion into zinc aluminates causes the peak shift towards higher wavenumber. The vibrational peaks at 1639 cm⁻¹ and 3480 cm⁻¹ indicates the intrinsic stretching mode of vibration belongs to hydroxyl molecules [37, 38]. The peak positioned at 2845 cm⁻¹ and 2929 cm⁻¹ represents the asymmetric vibrations of (carboxyl group) adsorbed atmospheric CO₂ [39].

3.6. VSM hysteresis loop analysis

Magnetic behavior of Zn₁₋ₓCuₓAl₂O₄ nanoparticles is determined by VSM analysis. VSM studies were performed at room temperature within −15 kOe to +15 kOe. Figure 7 shows the magnetic hysteresis curve for Zn₁₋ₓCuₓAl₂O₄ (0 ≤ x ≤ 0.5) nanoparticles. The hysteresis curve reveals the super paramagnetic nature of Zn₁₋ₓCuₓAl₂O₄ nanoparticles. Pure zinc aluminate samples exhibit the retentivity value 0.009 30 emu gm⁻¹ and coercivity value 161.72 Oe. These values indicate that the thermal variations are enough to dominate the anisotropic energy barrier of zinc aluminates and results in reverse the magnetization direction spontaneously [40, 41]. As seen in table 2, the retentivity (Mₘ) and coercivity (Hₘ) values show the fluctuations with respect to
Cu$^{2+}$ ion in Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ (0 $\leq$ x $\leq$ 0.5) nanoparticles. It is owing to the interaction among the oxygen and metal ions in the sublattice of the spinels. In addition, this variation in magnetic parameters is mainly due to cationic re-distribution (i.e. normal to inverse spinel) in different composition of copper dopants or absence of ordered spin in the surface [42, 43]. Hence, it is confirmed that the dopant (Cu$^{2+}$) atom play a major role to modify the magnetic behavior of the spinel nanoaluminates.

4. Conclusions

Microwave combustion method using L-alanine as fuel is adopted to synthesize pure and copper doped zinc (Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ (x = 0, 0.1, 0.3 and 0.5)) nanoaluminates. Powder XRD studies confirmed the single phase
cubic spinel of pure and Cu$^{2+}$ ion doped Zn aluminates. Lattice parameter and lattice strains continuously decrease as increase of copper ions is due to lattice contraction. HRSEM images reveal the agglomerated coalescence morphology. EDX spectra confirm the presence of Zn$^{2+}$, Cu$^{2+}$, Al$^{3+}$, O$^{2-}$ elements alone. It is found that the observed optical bandgap is in the range of 3.57–5.45 eV. From FTIR spectra, three prominent peaks suggested that the phase formation spinel nano aluminates. The fluctuations in magnetic retentivity ($M_r$) and coercivity ($H_c$) is owing to the cationic re-distributions between octahedral and tetrahedral sites. The magnetic and optical measurements of Zn$_{1-x}$Cu$_x$Al$_2$O$_4$ ($x = 0, 0.1, 0.3$ and $0.5$) nanoparticles make them suitable candidate for various applications like catalytic, sensor and optoelectronic devices.

**ORCID iDs**

N Iyandurai [https://orcid.org/0000-0003-2960-6316](https://orcid.org/0000-0003-2960-6316)

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