Syntheses of new spinels Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ nanocrystallines structure: Optical and magnetic characteristics

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A B S T R A C T
Nanocrystalline of ZnAl$_2$O$_4$ spinel was synthesized by employing the microwave combustion method. Different new spinel compositions of formula Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ (0.0 < x < 1.0) were prepared by substitution of Zn ions with Fe ions. The as-synthesized resultant material ZnAl$_2$O$_4$ with spinel structure as well as Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ compositions were characterized by Energy Dispersive X-ray and X-ray diffraction. Morphology and particle size evaluation of the nanoparticles were characterized by transmission electron microscopy images. The optical absorption spectra and the magnetization were measured at room temperature for each Fe ratio. The substitution effect of Fe ions on the optical and magnetic properties of the original spinel was studied. The optical absorbance showed that the optical band gap decreased with increasing Fe ratio.

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1. Introduction

Interest in the synthesis of nanoparticles has increased due to their different properties when compared to the corresponding bulk material. Spinel-type oxides Al$_2$O$_4$, where A represent the divalent cations which in normal spinel occupying tetrahedral sites in a face centred cubic (FCC) lattice of oxygen anions and B represents trivalent cations occupying the octahedral sites of the cubic crystal structure [1]. These materials are suitable for a wide range of applications, such as magnetic materials, catalysis and ceramics [2]. Spinel nanoparticles can be synthesized by several techniques such as sol–gel [3], co-precipitation [4], microwave combustion [5,6], hydrothermal [7], Penchini method [8,9].

Aluminum-based spinels are intriguing class of oxide ceramics which have important technological applications. In spinel ZnAl$_2$O$_4$ structure, Zn$^{2+}$ and Al$^{3+}$ cations occupy the tetrahedral and octahedral in FCC lattice of oxygen anions respectively. The ZnAl$_2$O$_4$ spinel has attracted considerable attention since it possesses desirable properties such as high thermal stability, high mechanical resistance, better diffusion and ductility, low temperature sinterability, good resistance to acids and bases and excellent optical transparency [10–16]. According to those properties, the ZnAl$_2$O$_4$ spinel was used as ceramic materials [10,11], electronic and optoelectronic devices [12–14], catalyst and catalytic support of transition metal [15,16]. Consistent with all of the applications, ultrafine ZnAl$_2$O$_4$ spinel nanoparticles with a narrow particle size distribution and a low degree of agglomeration are desirable.

Completely replacement of Zn by Fe in ZnAl$_2$O$_4$ results in FeAl$_2$O$_4$ spinel (hercynite) which is mineral with the spinel structure. Hercynite, which is a representative antiferromagnetic spinel, shows a magnetization regardless of the normal spinel [17].

This work aims to synthesize and characterize Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ (0.0 < x < 1.0) nanoparticles as new spinels by the combustion method. Also, the effect of Fe ions substituted Zn ions on the optical and magnetic properties of ZnAl$_2$O$_4$ nanoparticles was studied.

2. Experimental

2.1. Samples synthesizing

In the typical microwave combustion method for preparation of pure ZnAl$_2$O$_4$ spinel, all starting chemicals used in this study were pure grade Zn(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O. These chemicals were dissolved in double distilled water with glycine (NH$_2$CH$_2$COOH) as a combustion fuel at a fixed ratio 1:2:0.3 (according to their weights) to obtain a homogeneous solution. The
solution was placed in a microwave oven type [SHARP R-241R (W)] to improve the full reaction occurs as the water evaporates and the combustion takes place. After the combustion, a white dry foamy was generated and the resultant powder was collected to perform further analyses.

The synthesis of the composition Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ $(0.0 \leq x \leq 1.0)$ took almost the same steps as before but the starting materials were Zn(NO$_3$)$_2$$\cdot$6H$_2$O, Al(NO$_3$)$_3$$\cdot$9H$_2$O and Fe(NO$_3$)$_3$$\cdot$9H$_2$O using also glycine (NH$_2$CH$_2$COOH) as a combustion fuel at a fixed ration (1-x): x:2:0.3. The resultant powders were colored graduate from white to brown with increasing the ratio of Fe.

2.2. Characterization methods

The chemical composition of prepared samples was check by Energy-Dispersive X-Ray (EDX) Spectroscopy technique using scanning electron microscope model QUANTA FEG 250 (Field Emission Gun) attached with EDX unit with accelerating voltage 30 kV. X-ray diffraction (XRD) measurements were performed on Philips X-ray diffractometer model PW. 1710 with CuK$_\alpha$ radiation ($\lambda = 1.5405$ Å) with an operating applied voltage 40 kV and current 30 mA. Scanning rate was maintained at 0.06° per minute in the range of 2θ from 4° to 70°. The diffraction patterns of the prepared samples were compared with those reported in the database of the Powder Diffraction File (PDF) maintained in the International Centre for Diffraction Data (ICDD). The morphology of the prepared nanoparticles was investigated by high resolution transmission electron microscope (HRTEM-JEOL JEM 2100).

Infrared (IR) transmittance spectra of the samples were measured by Nicolet Fourier transformation infrared (FTIR) 6700 spectrometer using the KBr pellet method in the range 400–4000 cm$^{-1}$. Optical absorbance was measured for the powder suspension of the samples using Thermo Evolution 300 UV–Visible Spectrophotometer. The optical measurements were carried out between 200 and 900 nm. A Vibrating Sample Magnetometer (VSM, LakeShore 7400) was used to investigate the magnetic properties of Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ spinels at room temperature.

3. Results and discussion

3.1. Energy dispersive X-ray analysis

The chemical composition of prepared samples was check by Energy-Dispersive X-Ray (EDX) Spectroscopy technique. The results in Fig. 1 show the spectral distribution of ZnAl$_2$O$_4$ spinel sample and those of substituted with Fe ions. The spectral distribution of substituted samples indicates that the samples are consisted of O, Al, Zn and Fe only. No other elements were observed.

3.2. Structure and particle size

X-ray powder diffraction measurements were collected for the synthesized materials without any heat treatment. The diffraction patterns of the as prepared ZnAl$_2$O$_4$ and FeAl$_2$O$_4$ were illustrated in Figs. 2a and 3a. Comparing the diffraction patterns of Figs. 2a and 3a with those reported in the ICDD PDF files of Figs. 2b and 3b confirms the spinel cubic structure of synthesized ZnAl$_2$O$_4$ and FeAl$_2$O$_4$. However, the sharpness of the diffraction peaks in Figs. 2a and 3a indicates the good degree of crystallinity of the synthesized spinels.

The diffraction data of Fe substitution samples were illustrated in Fig. 4 showing that the samples were crystallized in preferential orientations indicated with different peaks. These orientations were along seven planes. The formation of cubic spinel aluminate structure was confirmed by the existence of diffraction planes of (220), (311), (400), (331), (422), (511) and (440). In particular, the presence of (440), (400) and (311) diffraction planes is an evidence for face-centred cubic spinel crystal. The strong XRD peaks of (220), (311) and (440) planes indicate these planes are the most preferential orientations. The assignment of the planes was determined on the basis of best agreement between the experimentally observed of inter-planar spacing and diffraction angles with those of ICDD.

The average particle size ($D_{av}$) in nm can be calculated using the Scherrer equation [18]:

$$D_{av} = \frac{K\lambda}{\beta \cos \theta}$$  (1)
Where $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half maximum (FWHM) in radians, $\theta$ is Bragg’s angle and $k$ is constant which assigned to 0.9. The calculated $D_{av}$ values for observed crystalline phases for each Fe ratio are listed in Table 1. Average lattice constant ($a$) is calculated as:

$$a = \sqrt{\frac{h^2 + k^2 + l^2}{2 \sin \theta}}$$  \hspace{1cm} (2)

The dislocation density ($\delta$) which represents the amount of defects in a given sample is defined as the length of dislocation lines per unit volume of the crystal; and it was calculated by the following equation [19]:

$$\delta = \frac{1}{D_{av}}$$  \hspace{1cm} (3)

The average internal lattice strain ($\epsilon$) was estimated using the following relation [20]:

$$\epsilon = \frac{\beta \cos \theta}{4}$$  \hspace{1cm} (4)

The theoretical density ($\rho$) for any material can be calculated from the XRD data based on the number of molecules per unit cell ($Z$) as follows [21]:

$$\rho = \frac{ZM}{Na^2}$$  \hspace{1cm} (5)

where $Z=8$ for aluminates and ferrite spinel, $M$ is the molecular weight of the material, $N_a$ is Avogadro’s number and $a$ is the lattice constant. The calculated values of $D_{av}$, $\delta$, $\epsilon$, and $\rho$ were listed in Table 1. From this Table, one notes that the value of $\rho$ decreases with increasing the ratio of Fe ions. That is because the atomic weight of the substituted iron (55.845 gm/mol) which is lower than that for zinc (65.38 gm/mol).

### 3.3. TEM analyses

High resolution transmission electron microscope (HR-TEM) was used to study the morphology of the prepared nanoparticles and to evaluate the crystallite grains microstructure. Fig. 5 shows the HR-TEM images of pure ZnAl$_2$O$_4$, Zn$_{0.5}$Fe$_{0.5}$Al$_2$O$_4$ and FeAl$_2$O$_4$ at magnification of 50 nm. The TEM images indicated the particles sizes were within the nanoscale range. The micrographs also showed irregular shaped particles with particle size distribution below 50 nm. The average particle size, $D_{av}$, was estimated from the TEM images by the so-called image j viewer software [22]. The calculated $D_{av}$ was found to be 13.55, 13.25 and 10.84 nm for ZnAl$_2$O$_4$, Zn$_{0.5}$Fe$_{0.5}$Al$_2$O$_4$ and FeAl$_2$O$_4$, respectively, which in agree with X-ray results. The corresponding selected area of electron diffraction (SAED) patterns was shown in Fig. 6. The ring patterns of

<table>
<thead>
<tr>
<th>Fe content</th>
<th>$D_{av}$ (nm)</th>
<th>$a$ (Å)</th>
<th>Vol. ($Å^3$)</th>
<th>$\delta \times 10^{-3}$ (nm$^{-2}$)</th>
<th>$\epsilon \times 10^{-2}$</th>
<th>$\rho$ (gm/cm$^3$)</th>
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<td>0.0</td>
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<td>535.19</td>
<td>5.323</td>
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<tr>
<td>0.1</td>
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<tr>
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<td>5.037</td>
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<td>11.222</td>
<td>3.889</td>
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</table>
SAED indicated the crystalline nature of the investigated samples. However, the observed of many spots contained by each ring was ascribed to the presence of large number of nanoparticles.

3.4. Infrared spectroscopy

The FTIR spectra for the samples were examined to study their functional groups. Fig. 7(a) shows the FTIR spectra of the Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ in the range 400–4000 cm$^{-1}$ and Fig. 7(b) shows the spectra in the range 450–850 cm$^{-1}$ which is the active region for the metal oxide bands. The spinel type structure can be confirmed by the bands at low energy (below 1000 cm$^{-1}$), which are related to the stretching and bending modes of Al–O bonds. If Al$^{3+}$ ions are in the octahedral sites of the six-coordinated AlO$_6$ groups, the structure subsequently is normal spinel and the stretching and bending vibrations are expected at 500–700 cm$^{-1}$ [23–26]. The observed three strong absorption bands at 499, 554, and 665 cm$^{-1}$ were assigned to the characteristic vibration bands of zinc aluminate spinel structure [25], in which, Al$^{3+}$ cations occupy the octahedral sites of a cubic lattice. The absorption bands at 1381 cm$^{-1}$ present in all composition can be attributed to the vibration modes of the groups originating from the organic compounds [25]. In all spectra, the observed bands at 1630 cm$^{-1}$ and 3447 cm$^{-1}$ were assigned to H$_2$O deformation vibration and the O–H stretching vibration of water molecules, respectively [25], which was due to the absorption of water from the atmosphere by the nanosized sample having high surface area [27].

3.5. Absorbance and optical gap

Significant information about the mechanism of the electronic transition and the optical band gap of different materials can be obtained by measuring the absorption spectra in the UV–Vis regions. The measured absorbance ($A$) for Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ ($0.0 \leq x \leq 1.0$) was shown in Fig. 8. The absorbance decreased with increasing the wavelength ($\lambda$) of the incident photons for all samples. The absorption coefficient ($\alpha$) was calculated from the absorbance, $A$, according to Beer-Lambert law [28]:

\[ \alpha = \frac{A}{cl} \]  

where $c$ and $l$ are the concentration and the length of the solution, respectively. The type of the optical transition and the optical band gap ($E_g$) can be determined using Tauc’s equation [29]:

\[ a\hbar \nu = B(\hbar \nu - E)^m \]

Where $\hbar \nu$ is the energy of the incident photons, $B$ is a constant and $m$ is an exponent characterizes the type of the optical transition. The exponent $m$ can take four values 1/2, 2 and 1/3, 3 for direct, indirect allowed transition and direct, indirect forbidden transition, respectively. Most semiconductors exhibit an allowed direct transition mechanism. For present dependent of $\alpha$ on $\hbar \nu$ in Fig. 9, it is noticed that the exponential like behavior and the linear portion that characterizes the optical band edge are clearly shown at the value of $m = 1/2$. The intercept of the fitting straight line with the x-axis reveals the $E_g$ value as shown in the inset of Fig. 9.

For pure ZnAl$_2$O$_4$, $E_g$ is 3.28 eV which is little lower than that previously reported where $E_g$ was 3.80 eV [30]. The dependence of $E_g$ on the Fe ion content in the studied compositions is shown in Fig. 10. The optical energy gap decreases linearly with increasing Fe content in the original spinel according to the empirical equation:
It has been observed that when the metal oxide ion of low $E_g$ added to other material of high $E_g$, the produced new energy band gap will have a value between the two materials [32]. The observed decrease in $E_g$ with adding of Fe ions could be attributed to the formation of new states at lower energy due to defects (vacancies) extant in the sample [33].

### 3.6. Magnetic properties

The magnetization curves for the Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ (0.0 ≤ $x$ ≤ 1.0) system at room temperature are shown in Fig. 11. From the figure it is cleared that the magnetization curves do not exhibit hysteresis behavior and the increasing Fe content leads the zinc aluminate to possess magnetic property. This means, an introducing of iron in the matrix of zinc aluminate leads to reverse diamagnetic zinc to 2.62 eV for pure FeAl$_2$O$_4$ in agreement with that reported by Halenius et al. [31].

$$E_g = (-0.6846 \pm 0.0300)x + (3.2596 \pm 0.0178),$$

reaching to 2.62 eV for pure FeAl$_2$O$_4$ in agreement with that reported by Halenius et al. [31].

It has been observed that when the metal oxide ion of low $E_g$ added to other material of high $E_g$, the produced new energy band gap will have a value between the two materials [32]. The observed decrease in $E_g$ with adding of Fe ions could be attributed to the formation of new states at lower energy due to defects (vacancies) extant in the sample [33].
of Fig. 11 can be divided into two parts: linear parts and curvature parts [35]. The linear parts are interpreted by the antiferromagnetic spontaneously revers the direction [34]. The magnetization curves anisotropy energy barrier, thus allowing the magnetization to are guides to the eye.

magnetic moments of zinc in the Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ behavior which has high magnetic moments instead of the lower part increases and that can be attributed to iron magnetism magnetic nature of Fe $^{+2}$.

Further adding of Fe cations, the curved part increases and that can be attributed to iron magnetism behavior which has high magnetic moments instead of the lower magnetic moments of zinc in the Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ spinel.

4. Conclusions

New spinels of Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ (0.0 ≤ x ≤ 1.0) nanoparticles were successfully prepared by microwave auto combustion method using glycine as a fuel. EDX and XRD analyses indicated the as-prepared powder have the spinel structure without any other impurities. HR-TEM revealed that the particle size of samples was in the range of nanoparticles which accorded with X-ray results. The absorption bands between 500 and 700 cm$^{-1}$ in FTIR spectra were assigned to the characteristic vibration bands of spinel structure. The results of absorption spectra in UV–Vis regions showed the energy band gap for pure ZnAl$_2$O$_4$ is 3.28 eV and decreases with increasing the ratio of Fe. VSM study showed that an introducing of iron in the matrix of zinc aluminate leads to converse diamagnetic zinc aluminate to superparamagnetic material.

Fig. 11. Magnetic moment of Zn$_{1-x}$Fe$_x$Al$_2$O$_4$ (0.1 ≤ x ≤ 1.0) nanoparticles. The solid lines are guides to the eye.

Table 2

<table>
<thead>
<tr>
<th>Fe content</th>
<th>$H_c$ (G)</th>
<th>$M_r \times 10^2$ (emu/gm)</th>
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References

