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RESEARCH ARTICLE

Phase analysis and magnet properties of $Zn_xFe_{(3-x)}O_4$ prepared by milling process

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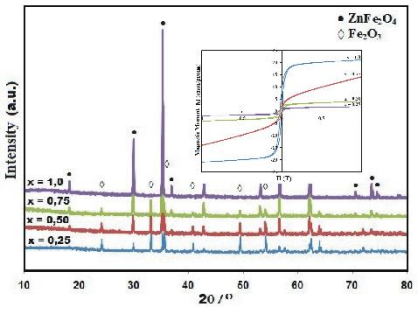
Graphical abstract



Abstract

Phase analysis and magnetic properties of $Zn_xFe_{(3-x)}O_4$ (x = 0.25; 0.50; 0.75 and 1.0) have been analyzed. The synthesis of $Zn_xFe_{(3-x)}O_4$ was carried out using a solid reaction with the $_xZnO : _{(3-x)}Fe_2O_3$ material composition (x = 0.25, 0.50, 0.75 and 1.0) according to the mole ratio of each, then being milled for 5 hours and sintered at a temperature of 1200 °C for 3 hours. Phase identification by XRD (X-ray Diffractometer) shows that $Zn_xFe_{(3-x)}O_4$ milling results form the diffraction peak of the $NiFe_2O_4$ and Fe_2O_3 phases, the greater the value of x (the Zn atom content) the less Fe_2O_3 % phase while the % phase $ZnFe_2O_4$ is getting bigger and even for x = 1.0 only $ZnFe_2O_4$ phase is formed ($ZnFe_2O_4$ formed 100% or single phase). Surface morphological observations with SEM (Scanning Electron Microscope) show the formation of an increasingly homogeneous structure along with the addition of Zn^{2+} ion content and varying sizes ranging from 1 µm to 100 nm. The properties magnetic of $ZnFe_2O_4$ with VSM (vibrating sample magnetometer) showed that the sample behave ferromagnetically with Ms higher (in the range 1.89 - 21.10 emu/g) while the Hc value is smaller (in the range 243 - 107 Oe) with the addition of Zn^{2+} ion content. Thus, the presence of the Fe_2O_3 phase can decrease the magnetic properties of the material.

Keywords: Crystal structure, zinc ferrite, magnet properties, milling process

INTRODUCTION

In recent years, researcher's attention to ferrite spinel nanoparticles has been increasing for industrial applications. The ferrite spinel nanoparticles with the structural formula of MFe_2O_4 (M is a divalent metal ion, such as Ni, Co, Cu, Mn, Mg, Zn, Fe) also have spinel cubic crystal structure [1]. Ferrite spinel nanoparticles have superior properties such as high electrical resistivity, high permeability, and eddy current losses that can be ignored by the propagation of high frequency electromagnetic waves. Its properties give it the potential to have aplications in data storage technology, microwave equipment, telecommunication equipment, drug delivery system, ferrofluid technology and gas sensor [2]. One of the ferrite spinel magnetic nanoparticles of interest today is the Zinc ferrite nanoparticles $ZnFe_2O_4$. This nanoparticle has an inverse spinel structure, is all Zn^{2+} ions are in the octahedral site and Fe^{3+} ions are distributed evenly on the tetrahedral and octahedral sites. The $ZnFe_2O_4$ nanoparticles show the ferromagnetic properties derived from the anti-parallel magnetic moment pair between the magnetic moment of the Fe^{3+} ion at the tetrahedral site with the magnetic moment of Zn^{2+} and Fe^{3+} ions at the octahedral site [3,4]. $ZnFe_2O_4$ nanoparticles are soft magnetic materials with low coercivity and saturation magnetization but have high electrical resistivity making them highly suitable for magnetic and magneto-optical applications. The $ZnFe_2O_4$ Nanopathic displays narrow hysteresis curves so that these materials are widely applied as gas sensors, catalysts, photocatalyst, microwaves and so on [5]. Various methods have been developed for the synthesis of $ZnFe_2O_4$ nanoparticles, such as solid reactions, sol-gel methods, coprecipitation methods, hydrothermal techniques and others [6,7]. In this study, $ZnFe_2O_4$ nanoparticles have been synthesized through solid reaction using milling technique. In the previous study, milling techniques using HEM *(High Energy Milling)* for 5 hours have been successfully synthesized $NiFe_2O_4$ spinel which has a single phase [8]. This method is choosen because the preparation is very simple and does not require a long time. It is expected that the results of this research can add information to obtain the properties of $ZnFe_2O_4$ nanoparticles effective for the purposes of it's application.

EXPERIMENTAL

Materials

The materials used in this study are ZnO powder from Merck with 99.9% purity, Fe_2O_3 powder with 99% purity. Equipment used, Thermoline furnace for heating $ZnFe_2O_4$ powder formed, XRD (*X-Ray Diffractometer*) brand PANalytical Empyrean for phase identification and structural analysis. Surface morphological observations were performed by JEOL JSM-6510 LA SEM *(Scanning Electron Microscope)*, and magnetic properties measurements by Oxford Tesla's VSM *(Vibrating Sample Magnetometer)* with 1 Tesla magnetization.

Synthesis of $Zn_xFe_{(3-x)}O_4$

$Zn_xFe_{(3-x)}O_4$ (x = 0.25, 0.50, 0.75 and 1.0) compounds are synthesized by solid reaction using milling technique. Fe_2O_3 and ZnO powders are each weighed in accordance with the mole ratio of a total

weight of 10 grams. The chemical composition for the $Zn_xFe_{(3-x)}O_4$ (x = 0.25, 0.50, 0.75 and 1.0) samples is synthesized according to the following reaction equation:

$$(3\text{-}x)Fe_2O_3 + 2xZnO \longrightarrow 2Zn_xFe_{(3-x)}O_4 \quad (1)$$

Each of these powder mixtures was inserted into the Stainless Steel vial and added a steel ball with weight ratio of the sample to the weight of the steel balls at 1 : 5 and 50 ml of ethanol solution was added. Furthermore, the process of milling each for 5 hours. The milled powders were dried at a temperature of 100 °C (for 2 hours). The dried powder was grinded and heated for 5 hours at 1200 °C. Crystalline phase were identified by XRD. The surface morphology was investigated by SEM and the magnetic properties of samples were measured with VSM. The research and characterization of the samples were conducted at the laboratory of the Center for Advanced Materials Science and Technology, BATAN.

RESULTS AND DISCUSSION

The synthesis of $Zn_xFe_{(3-x)}O_4$ (x = 0.25; 0.5; 0.75 and 1.0) by milling process using the HEM technique which is the solid state reaction has been done. The resulting diffraction pattern along with its relative intensity is matched to the diffraction pattern database named Crystallography Open Database (COD).

The result of the phase identification that has been done using the Match 3rd Edition software shown in Figure. 1 shows that for the values x = 0.25 to 0.75 indicates the presence of two main peaks at the angle of diffraction 2θ around the corner 32° and 35°, this indicates the second phase formation. The main peaks formed have the diffraction angle position and the intensity corresponding to the $ZnFe_2O_4$ and Fe_2O_3 phases. $ZnFe_2O_4$ phase compared to the crystallographic data from Crystallography Open Database (COD) with number 96-900-5113, while Fe_2O_3 phase compared with reference data number 96-901-5965. Based on the analysis of the formed phase it is known that, Fe_2O_3 phase has the highest relative intensity at the position of 2θ about 32° corresponding to the trigonal structure (104). The results of the analysis show that the peaks which are characteristic of the Fe_2O_3 phase are the tops of the plane (012) at an angle of about 24°, (104) at an angle of about 33°, (110) at an angle of about 36°, (113) at an angle of about 41°, (024) at an angle of about 49°, (018) at an angle of about 58°, (214) at an angle of about 61° and (300) at an angle of about 64° corresponding to the data reference from COD with number 96-901-5965. The $ZnFe_2O_4$ phase has the highest relative intensity at the 2θ position corner position at about 350 with the crystallographic area of [311] spinel-shaped cubic. This analysis is reinforced by the appearance of other peaks which are also characteristic of $ZnFe_2O_4$ is the top of the field 111 at an angle of about 18°, (220) at an angle of about 30°, (222) at an angle of about 37°, (400) at an angle about 42°, (422) at an angle of about 53°, (511) at an angle of about 56°, (440) at an angle of about 62° and (533) at an angle of about 73° corresponding to the reference data of the Crystallography Open Database (COD) with number 96-900-5113.

The diffraction peak at an angle of 32° is lower while the diffraction peak at an angle of 35° increases with the increase in the value of x, and even disappears in the sample with the composition of the value x = 1.0. The diffraction pattern for x = 1.0 is seen only one major peak ie the diffraction angle 2θ around the 35 ° angle which is the top of the field 311 of $ZnFe_2O_4$ indicates the indication of the formation of a single phase with a ferrite spinel structure having a cubic crystal structure with space group Fd3m with lattice parameter is a = b = c = 0,58836 nm at room temperature.

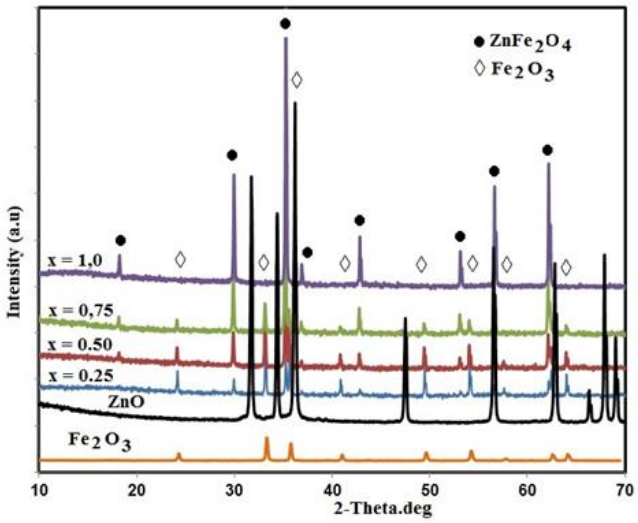


Fig. 1 XRD pattern of $Zn_xFe_{(3-x)}O_4$ powder (x = 0.25, 0.50, 0.75 and 1.0) milling result for 5 hours.

Table 1 Structure parameter, mass fraction, R factor and goodness of fit ($\chi 2$)

	x = 0.25	x = 0.50	x = 0.75	x = 1.0
	Phasa $ZnFe_2O_4$	**Phasa $ZnFe_2O_4$**	**Phasa $ZnFe_2O_4$**	**Phasa $ZnFe_2O_4$**
Crystal system	Cubic	Cubic	Cubic	Cubic
Space Group	Fd-3m (227)	Fd-3m (227)	Fd-3m (227)	Fd-3m (227)
Lattice Parameter (Å)	$a = b = c$ =8.4278 $\alpha = \beta = \gamma = 90^o$	$a = b = c$ = 8.4278 $\alpha = \beta = \gamma = 90^o$	$a = b = c$ = 8.4298 $\alpha = \beta = \gamma = 90^o$	$a = b = c$ = 8.4301 $\alpha = \beta = \gamma = 90^o$
V (Å^3)	598.624	598.972	599.052	599.117
ρ (gr.cm^{-3})	5.349	5.346	5.345	5.345
	Phasa Fe_2O_3	**Phasa Fe_2O_3**	**Phasa Fe_2O_3**	**Phasa Fe_2O_3**
Space Group	R -3 c	R -3 c	R -3 c	Not found
Crystal system	Trigonal	Trigonal	Trigonal	Not found
Lattice Parameter (Å)	a = b = 5.0284 c = 13.7269 $\alpha=\beta=90^o$ $\gamma = 120^o$	a = b = 5.0284 c = 13.7282 $\alpha=\beta=90^o$ $\gamma = 120^o$	a = b = 5.9205 c = 13,7294 $\alpha=\beta= 90^o$ $\gamma = 120^o$	Not found
V (Å^3)	300.593	300.620	300.771	Not found
ρ (gr.cm^{-3})	5.293	5.293	5.290	Not found
R Factor				
wRp	0.0284	0.0280	0.0270	0.0275
Rp	0.0221	0.0221	0.0215	0.0215
χ^2	1.330	1. 323	1.319	1.314

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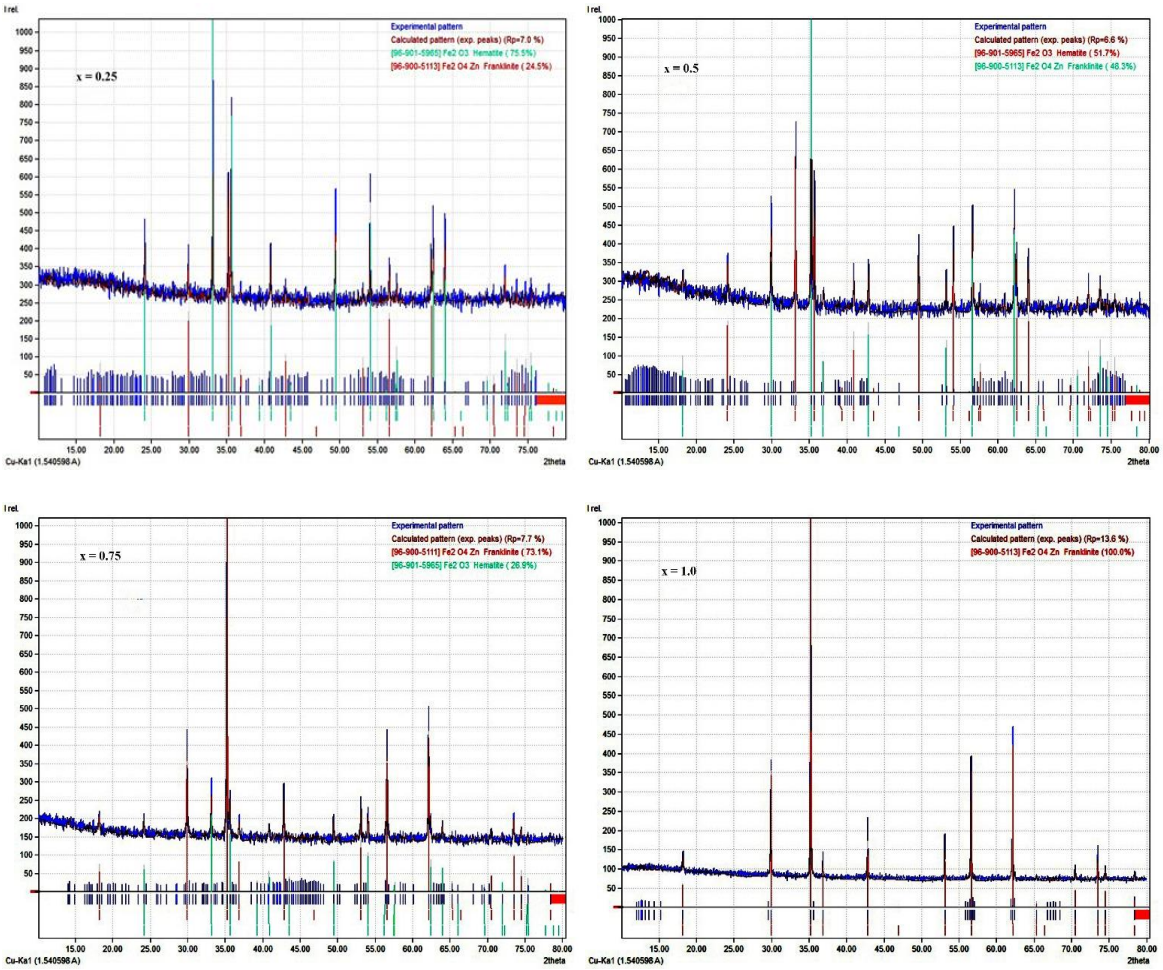

Fig. 2 Identificatian phase of ZnxFe(3-x)O4 powder (x = 0,25; 0,50; 0,75 and 1,0) milling result for 5 hours.

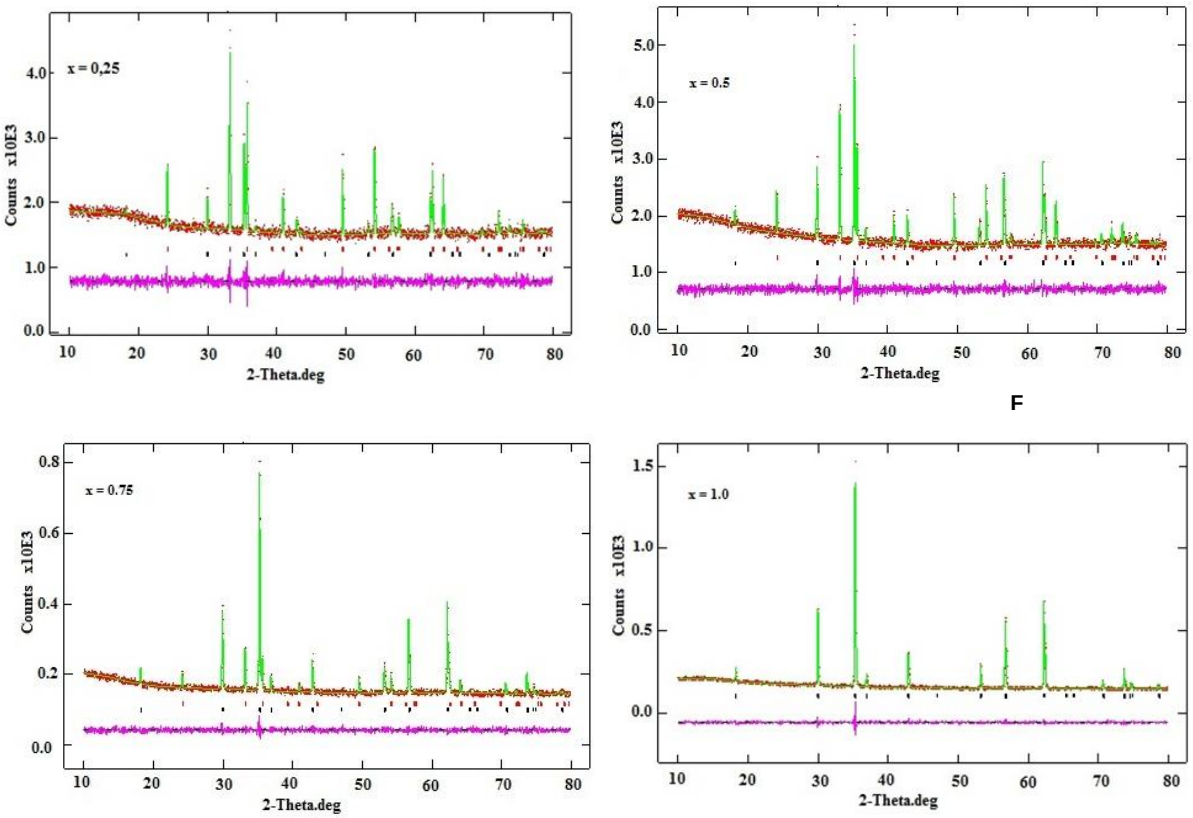

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Fig. 3 Refinement XRD pattern of $Zn_xFe_{(3-x)}O_4$ powder (x = 0.25, 0.50, 0.75, and 1.0) milling result for 5 hours.

Further analysis to show that the powders have multi phase for the value of x = 0.25 to 0.75 whereas for the value x = 1.0 is a single phase of $ZnFe_2O_4$. Figure 3 shows the refinement of the X-ray diffraction pattern of $Zn_xFe_{(3-x)}O_4$ (x = 0.25, 0.50, 0.75, and 1.0) powder results. The results of crystal structure analysis in the form of refinement fitting of X-ray diffraction pattern of $Zn_xFe_{(3-x)}O_4$ (x = 0.25 to 0.75) powder shows that multiphase peaks have been formed which belong to the phase of Fe_2O_3 and $ZnFe_2O_4$. As shown in Table 1, the results of this refinement resulted have an excellent fitting quality with a very small R factor. The R factor is the criteria of fit and the S factor is the goodness of fit which is of very small value. and according to Izumi the value of S or *χ2 (chi-squared)* is allowed to maximum 1.3 [13].

The result of observation of surface morphology of $Zn_xFe_{(3-x)}$ (x = 0.25, 0.50, 0.75, and 1.0) with SEM at 5000x magnification is shown in Figure 4. It shows that $Zn_xFe_{(3-x)}O_4$ powder with x = 0.25 to 0.75 has non-homogeneous particles and begins to homogeneously along with an increase in the value of x with a particle size in the range of from 300 nm to 1 µm. As for the value x = 1.0 looks homogeneous and uniform particles with a size of about 200 nm. In accordance with the results of observation by XRD that for x = 0.25 - 0.75 formed $ZnFe_2O_4$ phase and Fe_2O_3 phase. The Fe_2O_3 phase decreases with the increase of x value so that the particles formed are almost homogeneous.On the contrary, in the composition of x = 1.0 almost uniform shaped nanoparticles were formed. The greater homogenity in the composition of x = 1.0 happened due to the single-phase formation of $ZnFe_2O_4$ with spherical crystallite appearance. This results correspond with the research which has been done by Lazarevic who studied the formation of nano ferrites [14].

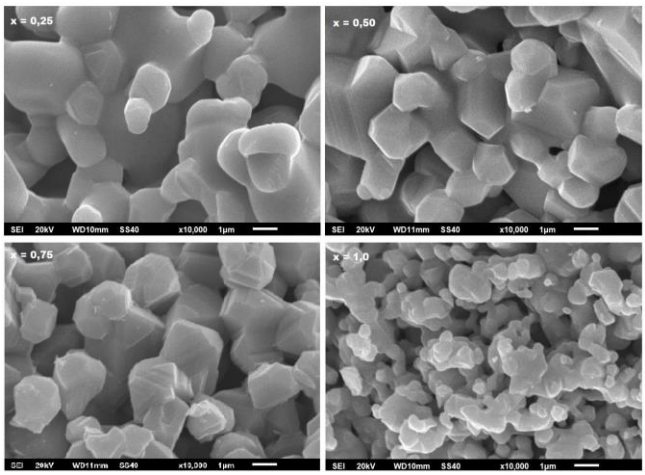

Fig. 4 SEM profile of $Zn_xFe_{(3-x)}O_4$ powder (x = 0.25; 0.50; 0.75 and 1.0) milling result for 5 hours.

The results of observation of $Zn_xFe_{(3-x)}O_4$ powder magnetic properties shown in Figure 5. Figure 5 shows the MH hysteresis curve in magnetic field range -1 Tesla to 1 Tesla. which gives information magnetization value of remanen (Mr). saturation magnetization (Ms) and the coercivity field (Hc).

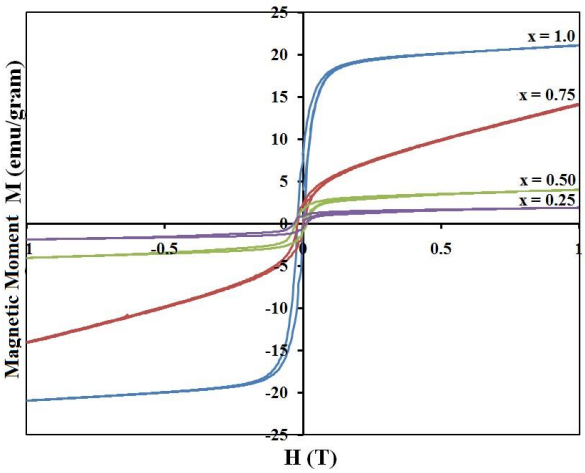

Fig. 5 M-H curva of $Zn_xFe_{(3-x)}O_4$ powder (x = 0.25; 0.50; 0.75 and 1.0) milling result for 5 hours.

The results of this observation indicate that all samples showed behavior of ferromagnetic properties with relatively small coercivity value. For more details. the hysteresis curve is magnified and the values of the magnetic parameters of each sample are shown in Table 2.

Table 2 Magnetic parameter of $Zn_xFe_{(3-x)}O_4$ powder (x = 0.25; 0.50; 0.75 and 1.0)

X	Sample	Value of Magnetic paramters		
		M_s (emu/g)	M_r (emu/g)	Hc (Oe)
0.25	$Zn_{0.25}Fe_{2.75}O_4$	1.89	0.84	243
0.50	$Zn_{0.50}Fe_{2.5}O_4$	4.03	1.59	200
0.75	$Zn_{0.75}Fe_{2.25}O_4$	14.10	2.16	131
1.00	$ZnFe_2O_4$	21.10	8.93	107

According to research results reported by Swamy et. al (2011) [1] and Xue et. al. (2007) [6] that $ZnFe_2O_4$ synthesized with combustion method showed Ms values of 7 emu / g and 20 emu / g respectively.

CONCLUSION

The single phase of $ZnFe_2O_4$ have succesfully synthesized in the composition of $Zn_xFe_{(3-x)}O_4$ for x = 1.0 and exhibit homogeneous morphological structure. This composition also has the best magnetic property among all compositions and exhibit ferrimagnetic behavior.

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