



**Original Research Article**

**Effects of Calcinations Temperature on the Synthesis, Chemical Structure, and Magnetic Properties of Nano Crystallites Zinc Ferrite Prepared by Combination of Sol-Gel Auto-Combustion and Ultrasonic Irradiation Techniques**

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**ABSTRACT**

Nanocomposite zinc ferrites were synthesized using glycine-nitrates by sol-gel auto-combustion technique. The influence of calcination temperatures varying from 400 to 900°C on structural and magnetic properties of spinel  $ZnFe_2O_4$  powders have been investigated. The characterization measurements including X-ray diffraction (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM) were performed for as-synthesized zinc ferrite particles. In brief, the effect of calcination temperature on magnetic behavior, demonstrated that, the magnitude saturation magnetization ( $M_s$ ) and remnant magnetization ( $M_r$ ) were decreased with the increasing temperature for synthesized samples. In turn, the coercivity ( $H_c$ ) and the shape of the hysteresis curve are affected significantly by calcination temperature. The coercivity ( $H_c$ ) is closely related to the microstructure, particle/grain size, shape of the pores of the crystals, and many other complex factors. The calcined sample at 400°C has the best magnetic properties with the highest  $M_s$  of 16.24 emu $g^{-1}$ , and with  $H_c$  of 102.79 Oe (at 10 kOe).

**Keywords:** Nanocomposite; ZnFe<sub>2</sub>O<sub>4</sub>; Calcination Temperature; Characterization; Magnetic Properties.

## 1. Introduction

Ferrite magnetic materials are among the most important materials used today in modern technology. They are used as an important part in many applications as in wave applications, radio electronics and sensors [1]. Many researchers studied the spinel oxides MFe<sub>2</sub>O<sub>4</sub> ferrites (where M is a divalent atom like Zn, Mg, Mn, Co, Ni etc.) [2]. Zinc Ferrite is of interest not only to basic research in magnetism, but also has great potential in technological application. ZnFe<sub>2</sub>O<sub>4</sub> is a promising semiconductor photocatalyst for various processes, due to its ability to absorb visible light and its high efficiency shows potentially wide applications in photo induced transformer, photoelectrochemical cells and photochemical hydrogen production [3-5].

It is worth mentioning that, the stable phase of zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>) possesses the normal spinel structure. The tetrahedral site is occupied by Zn<sup>2+</sup> because there is a very strong tendency for to prefer tetrahedral coordination in oxides with the spinel-type structure and Fe<sup>3+</sup> ions in the octahedral sites. However, in contrast to bulk compound, the nanocrystalline ZnFe<sub>2</sub>O<sub>4</sub> system always shows up as a mixed spinel in which Zn<sup>2+</sup> and Fe<sup>3+</sup> ions are distributed over the A and B-sites (tetrahedral and octahedral, respectively), therefore the formula is represented by



redistribution of iron ions at A and B sites (Fe<sub>A</sub><sup>3+</sup> - Fe<sub>B</sub><sup>3+</sup>), superexchange interaction is normally different from the (Zn<sub>A</sub><sup>2+</sup> - Fe<sub>B</sub><sup>3+</sup>) interaction, variation of the cation distribution over A and B sites in the spinel leads to different magnetic properties of these oxides even though the chemical composition of the compound remains the same [6]. There are two main factors which make nanomaterials to behave significantly different than that of bulk materials: (I) surface effects (causing smooth properties scaling due to the fraction of atoms at the surface) and (II) quantum effects (showing discontinuous behaviour due to quantum confinement effects in materials with delocalized electrons) [7]. The properties of these materials mainly depend on their shape, size and structure, which are strongly determined by the synthetic processes [8]. These factors affect the chemical reactivity of materials and physical properties such as; mechanical, optical, electrical and magnetic properties. Different methods have been adopted for the fabrication of ferrite nanoparticles such as dry- and wet-milling, sol-gel, co-precipitation, microemulsions.

Recently, Sol–gel auto combustion is a unique combination of the combustion and the chemical gelation processes [9]. This synthesis is an easy and convenient method for preparing ceramic and magnetic [10]. The main aim of present work is to prepare spinel  $ZnFe_2O_4$  powders and then study effect of calcination temperatures varying from 400 to 900°C on the magnetic properties of the prepared samples.

## 2. Experimental Section

### 2.1. Materials and Instrumentation

The dispersed  $ZnFe_2O_4$  powders were synthesized by sol-gel auto combustion technique. The raw materials used here in clouding zinc nitrate ( $Zn(NO_3)_2 \cdot 4H_2O$ ), ferric nitrate ( $Fe(NO_3)_3 \cdot 9H_2O$ ), glycine ( $C_2H_5NO_2$ ) and ammonia solution ( $NH_3 \cdot H_2O$ ) with analytical grade. All chemicals used were purchased from Merck (Germany) without further purification. De-ionized water was used in all experimental. In order to determine microstructure, chemical composition, the phase identification and average particles size were detected by XRD (Philips, XPERT- MPD, which operated 40 kV / 40mA) with  $Cu K_{\alpha}$  radiation in a wide range of Bragg's angle ( $20-100^{\circ}$ ) by 0.01 step size at room temperature. The morphology of particles was observed using SEM (Phillips, XL30). Ultrasonic irradiation (HF- 35 kHz/240W) made in Germany, which it is a powerful tool for the particles synthesis with controlled and uniform particle size. The Vibrating Sample Magnetometer (Kashan University) with a maximum field of 10 kOe was used to study the magnetic behaviour of the prepared nanocomposites.

### 2.2. Powder preparation

The appropriate amount of metal nitrates and glycine were dissolved into minimum deionized water to form mixed solutions (molar ratio of  $Zn^{2+}$ :  $Fe^{3+}$ : glycine was fixed 1:1:2). Ammonia was also slowly dropped into the solutions to change the pH value to 7. The solutions were heated at 60°C to form the sol, and then the solution was evaporated by heating at 60-65°C with continuous stirring until viscous gel was formed in the presence of  $N_2$  atmosphere. Increasing the temperature up to 350°C led to the ignition of the gel, until all the gel was burnt out completely to form a fluffy loose powder. The entire combustion process was done in a few minutes. Finally, the as-burnt powders were calcined in the furnace at 400–900° C for 3 h. After that, the products were placed in ultrasonic bath at 15°C for 20-25 minutes. Ultrasonic can effectively prevent the crystal growth and aggregation [11]

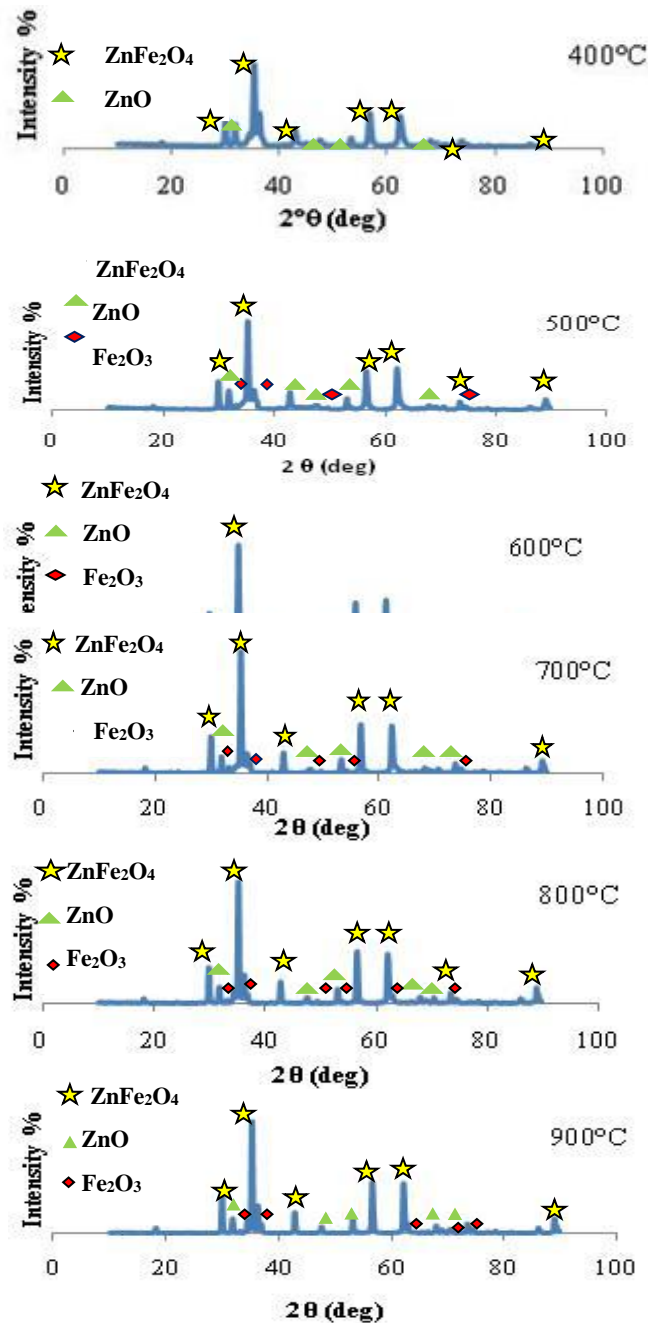
### 3. Results and discussion

#### 3.1. X-ray diffraction (XRD) analysis

The XRD patterns of the samples calcined at different temperatures varying from 400 to 900°C were shown in Figure 1 to investigate the influence of the calcination temperature on the structure. All of the diffraction peaks is confirmed the formation of the phases zinc ferrite with face centred cubic spinel and Fd3m (2 2 7) space group, Zincite with Hexagonal and p6<sub>3</sub> mc (1 8 6) space group and Hematite with Rhombohedral and R3c (1 6 7) space group. The average size of nanomaterials can be derived from the peak broadening (2 2 7) and calculated by using the Scherer's equation (1), provided that the nanocrystallites size is less than 100 nm.

$$D = (0.9 \lambda) / (\beta \cos \theta) \quad (1)$$

where D is the crystalline size,  $\lambda$  is the wavelength of X-ray radiation (Cu K $_{\alpha}$ ),  $\theta$  is the Bragg angle and  $\beta$  is the full width at half maximum (FWHM) of the most intense diffraction peak (2 2 7). The average size of as-prepared ZnFe<sub>2</sub>O<sub>4</sub> crystallites was evaluated according based on the obtained XRD data. The calculated average nanoparticles sizes at 400, 500, 600, 700, 800 and 900°C are 31, 45, 50, 69, 74 and 81 nm, respectively [11].



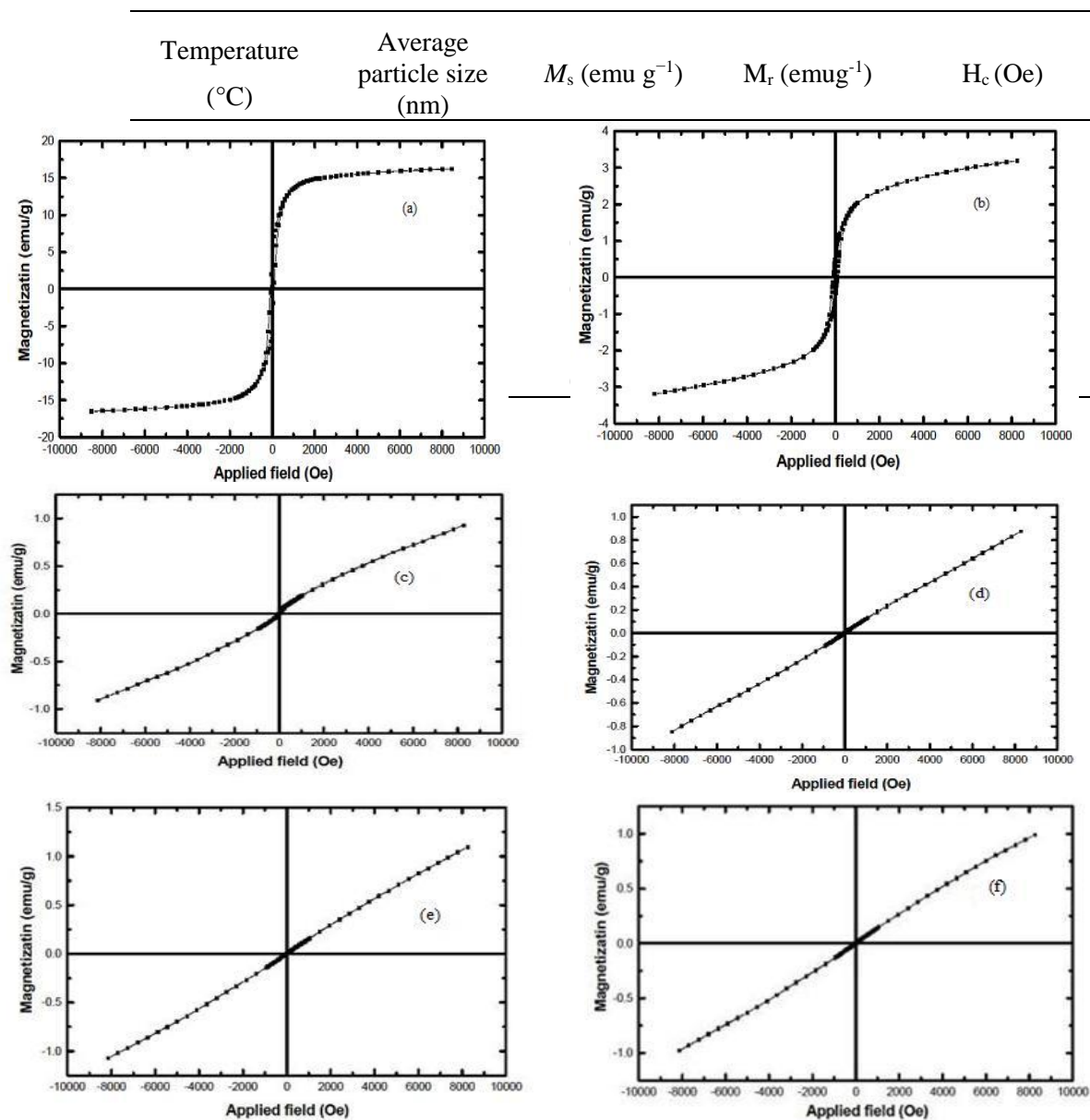
**Figure1.** XRD patterns of the zinc-ferrite samples calcined at different temperatures varying from 400 to 900°C.

### 3.2. Magnetic properties

To investigate the influence of the calcination temperature on magnetic properties of nanocomposite samples, hysteresis loops of samples calcined at different temperatures varying from 400 to 900°C were analyzed by VSM, that is shown in Figure 2. The magnetic properties

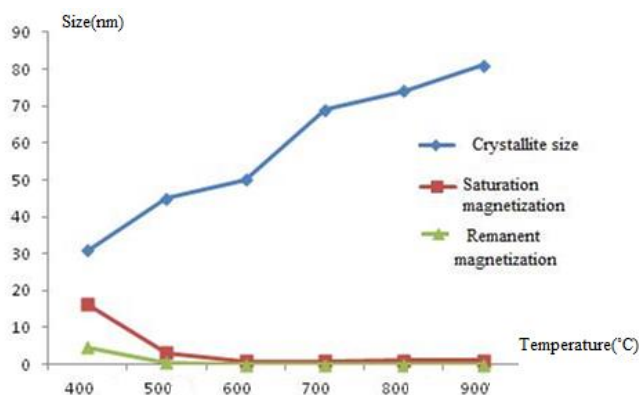
such as saturation magnetization  $M_s$ , remanence magnetization  $M_r$  and coercivity  $H_c$  are determined from the hysteresis loop and relevant data are collected in Table 1. The maximal magnetic field applied in the measurements is 10 kOe and the detection was carried out at room temperature.

**Table1.** Average particle size, crystallinity percent and magnetic parameters of samples calcined at different temperatures varying temperature from 400 to 900°C.



**Figure2.** hysteresis loops of samples calcined at different temperatures varying temperature from (a) 400 (b) 500 (c) 600 (d) 700 (e) 800 and (f) 900°C

The results revealed that, the calcination temperature control, as an efficient factor exerted direct influence on crystallite size, phase composition, and magnetic properties of the resultant particles. Briefly, temperature can affect on distribution and atomic thermal motions of cations in the  $\text{ZnFe}_2\text{O}_4$  nanocrystalline structure that led to change magnetic characteristics of these magnetic materials. It is well known that the increase in temperature of a solid result in an increase in the magnitude of the thermal vibrations of the atoms. As the atomic magnetic moments are free to rotate which tends to randomize the direction of any moment that may be aligned. When the temperature of magnetic materials increased the atomic thermal motions contract the coupling forces between the adjacent atomic dipole moments, causing some dipole misalignment. The saturation magnetization is determined only by the composition of the ferrite material. For example, in cubic ferrites, substitution of a divalent metal ion such as  $\text{Zn}^{2+}$  for  $\text{Fe}^{2+}$  in  $\text{FeO-Fe}_2\text{O}_3$  will change the saturation magnetization. The dependence of the magnitude saturation magnetization ( $M_s$ ), remanent magnetization ( $M_r$ ) and crystallite size as a function of the calcination temperature for prepared samples were shown in Figure 3. What should be especially noted is that the variation of  $H_c$  is different from of  $M_s$  and  $M_r$ . The coercivity ( $H_c$ ), the shape and width of the hysteresis loop of a ferrite depends not only on the chemical composition but also on various factors such as porosity, size and shape of the pores of the crystals [12].



**Figure3.** The dependence of the saturation magnetization ( $M_s$ ), remnant magnetization ( $M_r$ ) and crystallites size as a function of the calcination temperature for prepared samples at from 400 to 900°C.

The experimental observations showed the calcination temperature values have a direct influence on the produced crystallite size; i.e. the crystal size would change with the changing calcination temperature. One of the efficient factors in the changes magnetic properties of the samples can be attributed to the crystallite size and crystallinity.

The peaks in all XRD patterns confirmed the formation of  $\text{ZnFe}_2\text{O}_4$  phase at temperature from 400 to 900°C. The calcined sample at 400°C has the best magnetic properties with the highest  $M_s$  of 16.24 emu/g (at 10 kOe), and with coercivity  $H_c$  about 102.79Oe. The XRD results revealed the presence of  $\text{ZnFe}_2\text{O}_4$  and ZnO phases in the sample prepared at 400°C; whilst, at temperatures from 500 to 900°C, the  $\text{Fe}_2\text{O}_3$  phase could also be observed alongside the  $\text{ZnFe}_2\text{O}_4$  and ZnO phases. As  $M_s$  is determined only by the composition of the ferrite material, thus variations of  $M_s$  can be attributed to presence of  $\text{ZnFe}_2\text{O}_4$ , ZnO and  $\text{Fe}_2\text{O}_3$  phases; however, coercive force is closely related to the microstructure, particle/grain size, shape of the pores of the crystals, external molecular force of ions, and many other complex factors (Figure 3). The  $H_c$  value at 400, 500, 600, 700, 800 and 900°C are 102.79, 104.2, 57.80007, 47.26568, 52.34 and 41.16712, respectively. The experimental observations showed  $H_c$  decreases gradually with increasing calcination temperatures.

These samples have a low coercivity and are called soft ferrites. Zinc soft ferrites are the magnetic materials that do not retain their magnetism after being magnetized. These calcined samples are best described as disordered and highly dependent upon calcination temperature. The drastic drop of  $H_c$  For the sample calcined at 900°C might originate from the transition of magnetic single domain to magnetic multi-domain with in a particle [13].

#### 4. Conclusions

Nanocomposite zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ) powders have been synthesized successfully by sol-gel auto combustion. The particles have been calcined at temperatures varying from 400 to 900°C. The calcined sample at 400°C has the best magnetic properties with the highest  $M_s$  of 16.24 emu/g and with  $H_c$  of 102.79Oe (at 10 kOe), respectively. It is worth mentioned that, prepared sample at 400°C revealed presence of  $\text{ZnFe}_2\text{O}_4$  and ZnO phases, whilst, at temperatures from 500 to 900°C, the  $\text{Fe}_2\text{O}_3$  phase could also be observed alongside the  $\text{ZnFe}_2\text{O}_4$  and ZnO phases. The calcined samples are best described as disordered and highly dependent on temperature. The



influence increasing temperature on magnetic properties demonstrated that, the magnitude saturation magnetization and remnant magnetization decreased with increasing crystallites size for samples synthesized. Total result, magnetic properties of the ferrites depend on preparation method, the type and amount of constituent elements, particle size, microstructure, surface-to-volume ratio, and the calcination temperature.

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