The effects of synthesis conditions on the magnetic properties of zinc ferrite spinel nanoparticles

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Abstract. Zinc ferrite nanocrystals were synthesized from metal chloride precursors via chemical co-precipitation method, using different synthesis conditions. Characterization measurements including X-ray diffraction (XRD), transmission electron microscopy (TEM) and superconducting quantum device (SQUID) were used to study the influence of precursor’s concentration and reaction time on the crystalline structure, average sizes and magnetic properties of zinc ferrite nanoparticles. The transmission images show spherical, homogenous shape and particle size ranging from 16 to 22 nm. DC magnetization (2-300 K) measurements reveal a superparamagnetic behavior for the ZnFe2O4 samples with a blocking temperature in the range of 18-24 K. Our results demonstrate that magnetic properties of magnetic particles can be largely modified by just changing the reaction condition such as concentration and reaction time, which might be a useful way to design novel magnetic materials.

1. Introduction

Spinels with general formula AB2O4 are very important magnetic materials because of their interesting magnetic properties combined with chemical and thermal stability. Spinel oxides have long played an important role in various applications. In normal spinel AB2O4, A is generally a divalent cation occupying tetrahedral sites, while B is a trivalent cation occupying octahedral sites. In inverse spinels, half of B cations occupy the tetrahedral sites, and the formula is rewritten as B [AB] O4[1].

The zinc ferrite ZnFe2O4 is one of the iron based cubic spinel series (S.G. = Fd3m), show striking changes in its magnetic properties by reducing the grain size to the nanometer-sized range. Bulk zinc ferrite is a completely normal spinel structure with Zn ions in the tetrahedral or A sites and Fe ions in the octahedral or B sites. Due to antiferromagnetic (AFM) super-exchange interaction between B-B ions, bulk zinc ferrite is antiferromagnetic at T_N = 10 K[2]. However, when it is prepared in the nanoscale, the energy associated to the low particle size favors a mixed cation distribution in which the Zn2+ and Fe3+ ions are distributed among the A and B sites giving rise to the mixed spinel structure (Zn2+,Fe3+)2[Fe3+,Fe2+]3[O4]2-, where parentheses and square brackets denote the A and B sites, respectively and the x is the inversion degree[3].
Zinc ferrites spinels have been investigated extensively due to their potential and technological applications such as magnetic and optical materials, electronic, semiconductors, pigments, biomedicine, magnetic date storage, medical imaging, drug targeting, and catalysis [4-13]. Various synthesis methods, such as co-precipitation, sol-gel, micro-emulsions, thermal decomposition, and ultrasonic cavitation approach, have been reported to prepare nanometer-sized \( \left( \text{Zn}^{2+}_{1-x}\text{Fe}^{3+}_x \right) \left( \text{Fe}^{3+}_{2-x}\text{Fe}^{2+}_x \right) \text{O}_4^{2-} \) particles [14-18]. Here we report a simple method to prepare zinc ferrite nanoparticle by co-precipitation reaction that is a useful and attractive technique for the preparation of nanosized particles because of its advantages like good stoichiometric control and the production of ultrafine particles with low sintering temperature and smaller duration.

Concentration and reaction time of reaction mostly result in the appearance of the disorder of Zn and Fe ions over the tetrahedral and octahedral sites, which in turn lead to a significant variation of the magnetic properties. In this work, we have studied the influence of synthesis conditions (concentration and reaction time) in the structural and magnetic properties of zinc ferrite spinel nanoparticles. The phase structure, morphology and magnetic properties of as-prepared products were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and superconducting quantum interference device (SQUID).

2. Experimental details:

The co-precipitation processing for synthesis zinc ferrite nanoparticles is based on the following reaction:

\[
\text{ZnCl}_2 + 2 \text{FeCl}_3 + 8 \text{NaOH} \to \text{ZnFe}_2\text{O}_4 + 4 \text{H}_2\text{O} + 8 \text{NaCl}
\]

In this work, ZnFe\(_2\)O\(_4\) nanoparticles have been obtained using different conditions (Table 1). The required quantities of zinc chloride (ZnCl\(_2\), 99%) and iron chloride (FeCl\(_3\), 99%) solution are mixed in a stoichiometric proportion. The precursors were added in H\(_2\)O and mixed homogeneously to yield a uniform mixture of precursor at 80 °C for 40 min. Then, aqueous hydroxide sodium solution (NaOH) is added drip (pH of the medium 11). The reaction temperature is controlled at 100 °C. All samples were washing at several times with water and ethanol to remove the soluble salt, and finally drying at 70 °C overnight. The dried samples were subsequently annealed at 500 °C for 8h to get the desired nanoparticles.

| Sample Symbol | reaction time (min) | [ZnCl\(_2\)] (mol/l) | [FeCl\(_3\)] (mol/l) |
|---------------|---------------------|----------------------|----------------------|
| ZF1           | 15                  | 0.308                | 0.616                |
| ZF2           | 120                 | 0.308                | 0.616                |
| ZF3           | 15                  | 0.462                | 0.924                |
| ZF4           | 120                 | 0.462                | 0.924                |

Thermogravimetric/Differential Thermal Analysis (TG/DTA) equipment was used to determine the thermal decomposition and weight loss of the precursor powder, by varying the temperature from 25 °C up to 1000 °C with a heating rate of 10 °C/min. The structure and particle sizes of all samples were performed by X-ray diffraction (Model: D8 Discover Bruker AXS Detector 2D Hi-Star Turbo Source Rotating Anode X-Ray Cu). The morphology and particle size were observed by transmission electron microscopy (TEM) with an accelerating voltage of 200 kV, while the magnetic characterization was done by Magnetic Properties Measurement System (MPMS-7XL, Quantum Design).
The thermal characterization of all sample synthesized ZnFe$_2$O$_4$ powder has been done by TGA (Thermogravimetric Analyzer) analysis. The results of TGA measurements of ZnFe$_2$O$_4$ are shown in Fig. 1. It shows exothermic peaks at around 220 °C which may correspond to the removal of water from precursors. In Figure 1, there is no more weight loss above 500 °C, which indicates the formation of crystalline ZnFe$_2$O$_4$ ferrite.

![Figure 1. TG–DTG curves of as-prepared ZnFe$_2$O$_4$ precursor powders (ZF1), (ZF2), (ZF3) and (ZF4).](image)

3. Results and discussion
The X-ray diffraction of (ZF1), (ZF2), (ZF3) and (ZF4) samples annealed at 500 °C for 8 h reveal that all the samples crystallized with the cubic spinel type structure, space group Fd3m, and permit us to exclude the presence of any impurities or secondary phases (Figure 2).
The lattice constant ($a$) was calculated from the XRD spectra using the following relation:

$$a = \left[ a^2 \left( h^2 + k^2 + l^2 \right) \right]^{1/3}$$

From Table 2, it can be observed that ZF1 and ZF3 nanoparticles samples show a higher unit cell parameter comparing with ZF2 and ZF4 samples ($a_{ZF1} = 8.47$ Å, $a_{ZF3} = 8.45$ Å). This variation could be related to disorder of cation distribution. So the reaction time affects directly the unit cell parameter of zinc ferrite sample.

The broadening of the reflections indicates the nanometric size of the particles for all samples. The average particle size ($D_{RX}$) has been calculated using the well-known Scherrer’s formula\cite{19},

$$D_{RX} = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where $\lambda$ is the wavelength (Cu K$_\alpha$), $\beta$ is the full width to half maximum (FWHM) of line broadening and $\theta$ is the Bragg angle of diffraction. The most intense peaks (311) are used to estimate the size of nanocrystallites and are found in the range of 12-16 nm (Table 2).

The average grain sizes of various ZnFe$_2$O$_4$ ferrites nanoparticles prepared with different synthesis conditions are listed in Table 2. It is observed that the average grain size decreases with increasing of reaction time, these results can be explained by the cations distribution between A and B sites.

The TEM micrographs for (ZF1), (ZF2), (ZF3) and (ZF4) samples are shown in Figure 2. The particles are regular and uniform in size. The average particles size is 21.6, 20.2, 21.2 and 16.4 for (ZF1), (ZF2), (ZF3) and (ZF4), respectively, which is in good agreement with the particle sizes estimated by Scherer’s formula (the same scale of variation).
Table 2. Lattice parameter (\(a\)), crystallites sizes (D) of samples (ZF1), (ZF2), (ZF3) and (ZF4).

| Sample | ZF1 | ZF2 | ZF3 | ZF4 |
|--------|-----|-----|-----|-----|
| \(a\) (Å) | 8.47 | 8.40 | 8.45 | 8.40 |
| \(D_{XRD}\) (nm) | 15.8 | 14.4 | 15.5 | 12.7 |
| \(D_{TEM}\) (nm) | 21.6 | 20.2 | 21.2 | 16.4 |

Figure 3. The TEM micrograph of samples (ZF1), (ZF2), (ZF3) and (ZF4).

The magnetic properties of the materials which originate from the quantum couplings at the atomic level, including the coupling between electron spins (S–S coupling) and the coupling between the electron spin and the angular momentum of the electron orbital (L–S coupling). Each of the magnetic nanoparticles tends to possess a single magnetic domain [20]. Therefore, the nanoparticles provide excellent opportunities for the fundamental studies on the relationship between magnetic behavior and the magnetic couplings at the atomic level.

Figure 4 shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves for (ZF1), (ZF2), (ZF3) and (ZF4) zinc ferritenanoparticles measured in the temperature range from 5 to 300 K. As expected, the ZFC magnetization increases before reaching a maximum value, that is, the blocking temperature (\(T_B\)) [21]. It is interesting to note that the tow curves diverge below this temperature. At temperatures above \(T_B\), the thermal energy, characterized by \(k_B T\),
is larger than the magnetic energy barrier and thus the materials become superparamagnetic following the Curie-Weiss law.

![Figure 4. ZFC-FC curves for the obtained samples ZnFe$_2$O$_4$ nanoparticles (ZF1), (ZF2), (ZF3) and (ZF4).](image)

The blocking temperatures $T_B$ of zinc ferrite nanoparticles are found to be approximately 20, 24, 18 and 22 for (ZF1), (ZF2), (ZF3) and (ZF4), respectively (Table.3). The magnetic anisotropy constant $K$ of the samples as-prepared can be calculated by the following formula:

$$K = \frac{25K_B T_B}{V}$$

Where $K_B$ is the Boltzmann constant ($K_B = 1.381 \times 10^{-23}$), $T_B$ is the blocking temperature of the samples, and $V$ is the volume of a single particle. The calculated magnetic anisotropy constant of our samples are given in Table.3. The $T_B$ is controlled by the anisotropy energy that is the result of contributions from both anisotropy constant and the particle size. The anisotropy constant is influenced by the inversion parameter that, as mentioned before, increases when the particle size decreases but also affected by the synthesis conditions (concentration and reaction time).

The field dependence of the magnetization of the as-prepared zinc ferrite nanoparticles was measured at 5K with an applied field $0 \text{Oe} \leq H \leq 6 \text{kOe}$. Figure.5 presents the magnetization curves of (ZF1), (ZF2), (ZF3) and (ZF4) samples. As shown in Figure.5 and Table.3, the values of $M_s$ are 45.4, 49.8, 46.6 and 49.7 emu/g corresponding to the (ZF1), (ZF2), (ZF3) and (ZF4) samples, respectively. The ZF2, ZF4 samples have highest $M_s$ values than the ZF1 and ZF3 samples, which can explained through the highest inversion degree. So, it is possible to increase the cations distribution between A and B sites if the reaction is maintained for a long time.
Figure 5. The magnetization \( M \) (emu/g) versus the applied magnetic field \( H \) (Oe) at 5K for all the obtained samples ZnFe\(_2\)O\(_4\) nanoparticles (ZF1), (ZF2), (ZF3) and (ZF4).

Table 3. Blocking temperature \( T_B \), magnetic anisotropy constant \( K \), Saturation magnetization \( M_s \), and Curie temperature \( T_C \) of (ZF1), (ZF2), (ZF3) and (ZF4) samples.

| Sample  | ZF1 | ZF2 | ZF3 | ZF4 |
|---------|-----|-----|-----|-----|
| \( T_B \) (K) | 20  | 24  | 18  | 22  |
| \( K \times 10^5 \) (ergs/cm\(^3\)) | 0.33 | 0.53 | 0.31 | 0.7 |
| \( M_s \) (emu/g) | 45.4 | 49.8 | 46.6 | 49.7 |

4. Conclusion

The zinc ferrites nanoparticles were prepared via co-precipitation method. XRD studies of products have proved the formation of cubic spinel structure, single phase, for all samples. Particles sizes as estimated using transmission electronic microscopy were found in the range 16–22 nm. The magnetic measurements show that all the samples exhibit a superparamagnetic behavior with a blocking temperature between 18 and 24 K. The results obtained reveal that the magnetic properties of zinc ferrite nanoparticles can be largely modified by the variation of synthesis condition such as concentration and reaction time, which might be a useful way to design novel magnetic materials for potential applications.
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