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Synthesis and characterization of $Fe_{0.6}Zn_{0.4}Fe_2O_4$ ferrite magnetic nanoclusters using simple thermal decomposition method

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ABSTRACT

This paper presents experimental results regarding the effect of the quantity of solvent on formation of the Fe–Zn ferrite nanoparticles during thermal decomposition. A ternary system of $Fe_{0.6}Zn_{0.4}Fe_2O_4$ has been synthesized by a thermal decomposition method using metal acetylacetonate in high temperature boiling point solvent and oleic acid. The X-ray diffraction study was used to determine phase purity, crystal structure, and average crystallite size of iron–zinc ferrite nanoparticles. The average crystallite size of nanoparticles was increased from 13 nm to 37 nm as a result of reducing the solvent from 30 ml to 10 ml in a synthesis batch. The diameter of particles and morphology of the particles were determined by transmission electron microscopy (TEM) and field emission scanning electron microscope (FESEM). Mid and far Fourier transform infrared (FT-IR) measurement confirmed monophasic spinel structure of ferrite. Furthermore, the DC magnetic properties of the samples were studied using the vibrating sample magnetometer (VSM). The largest Fe–Zn ferrite nanoparticles exhibited a relatively high saturation magnetization of 96 emu/g. Moreover, Low-field AC susceptibility measurement indicated blocking temperature of nanoparticles around 170–200 K.

1. Introduction

In recent years, magnetic nanoparticles have attracted increasing attention in biomedical fields thanks to their unique properties, including large surface area, nanosized stability, and controllability by external magnetic fields [1,2]. Nanotechnology provides for synthesizing materials in nano-dimensions where the classic laws of physics do not apply [3]. As the size of a particle decreases, the ratio of the surface area to the volume of the particle increases. For nanoparticles, this ratio becomes significantly large causing a large percentage of the atoms to reside on the surface compared to those in the core of the particle; this could affect material properties [4] especially in ferromagnetic materials where the decrease in the size of nanoparticles, could change magnetic properties [5]. The size of a magnetic nanoparticle is similar to the size of a magnetic domain, which is an absolutely novel phenomenology with regard to the bulk magnetic materials; therefore it can be stated that the magnetic properties of a given magnetic nanoparticle depend on the size of it [6]. For a sphere magnetic particle holding two semi-sphere domains, the energy of a domain wall is defined as $E = 4\sqrt{AK}\pi R^2$. Where A, K and R parameters denote the exchange interaction, radius and the anisotropy constant, respectively [7]. In a very small particle, energy of domain walls is very low, and the system does not have any tendency to create domains in the particle, therefore, such a particle turns into a single magnetic domain with a single moment [8]. These moments couple atomic spins that can be aligned using an external magnetic field [9].

If the interaction between the magnetic particles is very low, then, the magnetic moments of the particles will be independent of each other.

Each moment fluctuates thermally between easy directions and, as the temperature decreases, blocks according to the anisotropy energy barrier (superparamagnetic, SP, relaxation).

The *M–H* loop properties of magnetic nanoparticles at a constant temperature, are influenced by the ratio τ/t, where t is the time after removing the field. So, the time dependence of the magnetic remanence can be written as:

$$M_{r,t}/M_{r,o} = \exp(-t/\tau). \quad (1)$$

Superparamagnetic behavior can be achieved when $\tau/t \leq 1$. But, with increase in the value of τ/t, the behavior of magnetic nanoparticles changes and the magnetic remanence increases quickly with particle volume [10].

Another element that can affect magnetic properties is the atomic arrangement in crystal structures [9]. The magnetite crystalizes the cubic spinel structures with general formula AB_2O_4 for which there are three types of spinel arrangements:

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– *A* cations occupy tetrahedral positions and *B* cations occupy octahedral sites in the normal spinel.
– The second arrangement which is known as *inverse spinel*: *A* cations are located in half of the octahedral sites and *B* cations located in the other half of the sites as well as all of the tetrahedral positions.
– The third arrangement of cations in spinel structures contains a mixed arrangement of normal and inverse spinels i.e. the tetrahedral sites are filled by A and B cations, while remaining cations occupy octahedral sites [11,12].

It has been proven that ferrite nanoparticles with identical composition could be of different magnetic properties depending on the preparation method [4]. Magnetic nanoparticles are synthesized using various methods such as co-precipitation[13], microwave [14], normal and reverse microemulsion [15,16], sol–gel [17], hydrothermal process [18], combustion [19], high-energy ball milling [20], and the thermal decomposition method [21,22]. From fundamental and technological reasons, monodispersed magnetic nanoparticles were so interesting [23]. Also thermal decomposition can produce monodisperse nanoparticles with good size control, narrow size distribution and good crystallinity of magnetic nanoparticles [24]. So that, in this study, $Fe_{0.6}Zn_{0.4}Fe_2O_4$ nanoparticles have been prepared at high temperature under different solvent concentrations using the thermal decomposition method. In this work, magnetic and structural properties of $Fe_{0.6}Zn_{0.4}Fe_2O_4$ nanoparticles are examined and presented.

2. Experimental method

2.1. Materials

Zinc(II) acetylacetonate ($Zn(acac)_2$) and Iron(III) acetylacetonate ($Fe(acac)_3$) were purchased from E. Merck Co. and other solutions such as oleic acid and benzyl ether were obtained from Sigma Aldrich Co. and organic solvents such as methanol, acetone, hexane, chloroform, and ethanol were purchased from Samchun. All chemicals were used as received without any further purification.

2.2. Synthesis

In this case, the synthesis of $Fe_{0.6}Zn_{0.4}Fe_2O_4$ nanoclusters was a reform of a previously described method [25,26]. In a typical experiment for synthesis of Fe–Zn ferrite, Fe(III) acetylacetonate (2.60 mmol), and Zn(II) acetylacetonate (0.40 mmol) were mixed with benzyl ether (30 mL) and oleic acid (1.7 mL, 4.00 mmol) in a 250 mL three-neck flask to form a homogeneous solution. The flask was evacuated three times using a vacuum Schlenk line and refilled with nitrogen. Then, this mixture was heated to 110 °C and degassed at this temperature for 1 h. With change in the amount of solvent, the size of magnetic nanoparticles can be changed, so, in this article 3 batches include 10 mL (F1), 20 mL (F2) and 30 mL (F3) of benzyl ether were used. The solution was heated to the reflux temperature of the solution at the rate of 20 °C/min with vigorous magnetic stirring. The reaction mixture was maintained at this temperature for 30 min. After refluxing, the solution was cooled to the room temperature, and a mixture of toluene (40 ml) and hexane (10 ml) was added to the solution. Using the magnetic decantation technique, magnetic nanoclusters were separated and washed three times by a mixture of chloroform/methane and redispersed in chloroform (or left to dry overnight for the case of the magnetic and structural characterization measurements).

2.3. Characterization

X-Ray powder diffraction patterns were recorded on a Philips X-ray diffractometer with Co-K_α radiation ($\lambda = 1.78901$ Å). The scans of the selected diffraction peaks were carried out in step mode (step size 0.02°, measurement time 2 s, measurement temperature 25 °C, and standard: Si powder). For obtaining the correct value of crystallite size and lattice parameter X-ray diffraction patterns were processed by the computer software Materials Studio in the Rietveld method [27]. FESEM study was carried out in a TESCAN field emission type scanning electron microscope at 10 kV. The Fourier transform infrared spectroscopy (FTIR) in far spectrum was recorded as (KBr) discs in the range 700–150 cm^{-1} and in mid spectrum in the range of 4000–400 cm^{-1} using Perkin Elmer FTIR, 1403 spectrophotometer. Samples for TEM were prepared by drying the nanocluster solutions on amorphous carbon-coated copper grid and imaged by a CM30 Philips transmission electron microscopy at 150 kV. The magnetic measurements of the prepared powder were conducted at room temperature using the vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co., Kashan, Iran). The AC susceptibility measurements were carried out in the frequency range 33–666 Hz by using a Lake Shore AC Susceptometer, Model 7000. So, the nanoparticles were prepared in to a disk shape. Then, 10 Oe AC magnetic field was applied to the samples which were placed in the sample holder.

3. Results and discussion

In this study, sizes of magnetic nanoparticles have been controlled by changing the volume of the solvent in the thermal decomposition reaction. The benzyl ether act as a control agent for particle growth. However, the role of organic species is very complicated. Oleic acid provides the oxygen for the formation of the metal oxide, and also acts as capping agent. Such organic solvents can bind to particles' surfaces, and limit particle growth rate [28]. Fig. 1 shows an overall scheme leading to the formation magnetic nanoparticles synthesized by this technique.

The synthesis of monodispersed magnetic nanoparticles is influenced by the precise separation of nucleation and growth period [29]. However, some reaction equations based on calculation and analytical methods, have been proposed for the thermal

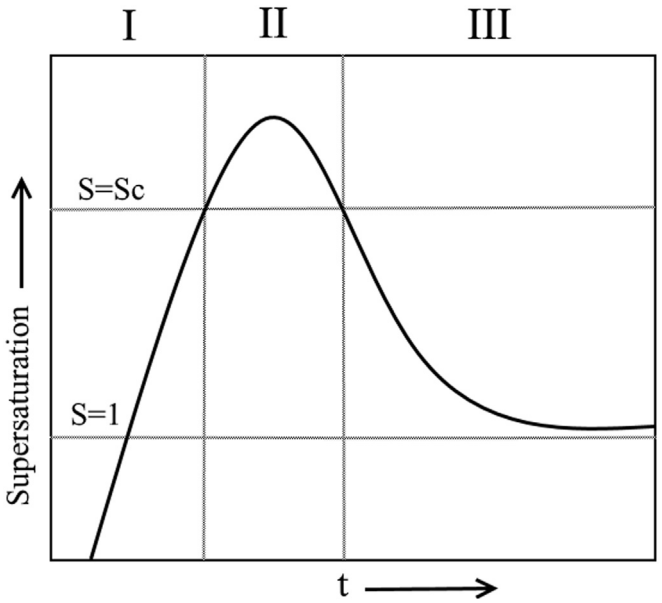

Fig. 1. LaMer plot: change of supersaturation versus time of the reaction.