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Determination of magnetic properties of nano-size $CoFe_2O_4$ particles synthesized by combination of sol-gel auto-combustion and ultrasonic irradiation techniques

S. Abedini Khorrami[1], G. Mahmoudzadeh[1], S. S. Madani[1,*], S. S. Sepehr[1], S. Manie[1], Sh. Moradi[1], F. Gharib[2], A. Mehrdad Sharif[1], P. Abromand Azar[3]

[1]*Chemistry Department, North Tehran Branch, Islamic Azad University, Tehran, Iran.*
[2]*Chemistry Department, Shahid Beheshti University, Tehran, Iran.*
[3]*Chemistry Department, Science and Research Branch, Islamic Azad University, Tehran, Iran.*

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Abstract

Nano-crystalline $CoFe_2O_4$ powder was prepared by combination of sol-gel auto-combustion and ultrasonic irradiation methods from metal nitrades and glycine. The resulting powders were investigated using X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM). The grains observed in as-burnt powder were proved to be $CoFe_2O_4$ nano-crystallites with high dispersibility and low agglomeration. The crystallite size of as-formed powders was 39.12 nm. The crystalline cobalt ferrite powders with magnetic properties having a maximum saturation magnetization (44.02 emu/g) was achieved for Fe^{3+}/Co^{2+} molar ratio 1:1 and calcination temperature 750°C for 4 h. Our results indicate that this method might provide a promising option for synthesizing high-quality $CoFe_2O_4$ nano-powder.

***PACs*:** 61.46.Df; 75.47.Lx; 61.64.Hk; 75.75.Fk
Keywords: *Nano-crystalline; $CoFe_2O_4$; Sol-gel auto-combustion; Ultrasonic irradiation; Magnetic properties*

1. Introduction

Nano-sized spinel ferrite particles currently receive considerable attention during the past several years because of their interesting magnetic properties [1–3]. It is found that when the particle diameter reduced to a definite size, spinel ferrite nano-particles may exhibit the so-called superparamagnetic properties, which is of great interest in macroscopic quantum tunneling of spin states [4]. Among the magnetic particles, cobalt ferrite ($CoFe_2O_4$) is a well-known hard magnetic material. The high coercivity [5] and moderate magnetization [6] makes $CoFe_2O_4$ a good candidate for many applications. The remarkable properties such as high saturation magnetization, high coercivity, strong anisotropy along with good mechanical hardness and chemical stability are not observed in the bulk sample [7]. These properties, along with their great physical and chemical stability, make $CoFe_2O_4$ nanoparticles suitable for magnetic recording applications such as audio and video tape and high-density digital recording disks [8,9].

The structure of the spinel $CoFe_2O_4$, on the other hand, crystallizes in a face-centered cubic structure with a large unit cell containing eight formula units. There are two kinds of lattices for cation occupancy, mainly A and B sites having tetrahedral and octahedral coordination, respectively. In the normal spinel structure Co is a divalent atom, occupying tetrahedral A sites, while Fe is a trivalent atom, sitting on the octahedral B sites. Since the Fe_A^{3+}- Fe_B^{3+} superexchange interaction is normally different from the Co_A^{2+}- Fe_B^{3+} 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. Cation distribution in octahedral and tetrahedral sites of ferromagnetic spinel $CoFe_2O_4$ has been studied for two extremes: quenched and slowly cooled samples, respectively [10,11]. There are several different synthesis methods used to generate ferrites as reported in the literature including sol–gel [12,13], coprecipitation [14,15], hydrothermal [16,17], mechano-chemical [18], refluxing [19] and precursor [20] methods. Recently, a sol–gel auto-combustion method has attracted much attention due to its inherent advantages of low processing temperature, homo-geneous reactant distribution, the products obtained by this method exhibit high crystalline quality, narrow size distribution and uniform shape [21].

Ultrasonic cavitation chemistry, an approach for synthesizing a variety of compounds at milder conditions is already the rage in materials technology. Over the last few years, this technique has also started to catch on in the materials science community as a way to speed discoveries in this area. The major

*Corresponding author: Sepideh Sadat Madani;
E-mail: se_madani@yahoo.com
Tel: (+98) 912 2709240
Fax: (+98) 21 22222512

advantage of this new method is that it affords a reliable and facile route for the control of both the synthetic process and nanostructure in advanced materials. Also, this process provides chemical homogeneity and reactivity through atomic level mixing within the precursor system, and phase pure crystalline materials can be prepared by calcining at reduced temperatures [22].

In this paper, we have presented the synthesis of cobalt ferrite ($CoFe_2O_4$) nano-particles by combination of sol-gel auto-combustion and ultrasonic irradiation methods followed by heat treatment at 750 °C. The size and morphology of the particles prepared by this method was studied by XRD and SEM, respectively. Finally, magnetic properties of the particles have been studied by VSM.

2. Experimental methods

2.1. Materials and equipments

Cobalt nitrade hexa hydrate ($Co(NO_3)_2.6H_2O$, Merck), iron nitrate nona hydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Merck), glycine ($C_2H_5NO_2$, Merck) and NH_4OH (Merck) was obtained with analytical grade. All materials were used without further purification. Deionized water was used for all experiments.

$CoFe_2O_4$ powders were synthesized from sol-gel auto combustion by ultrasonic irradiation (HF-Frequenz 35 kHz, 240W/ Germany) method. The phase identification of the burnt powder of $CoFe_2O_4$ is done using XRD (XPERT- MPD, Philips, operated at 40 kV and 40mA) in 2θ range from 20° to 100° by 0.02 step size. The structural morphology is investigated using SEM (Phillips L30 with 16 kV operating voltage). Magnetic properties of cobalt ferrite nanoparticles were studied by VSM (Made in Kashan University).

2.2. Preparation of cobalt ferrite nano-crystals

Nano-crystalline cobalt ferrite was prepared by combination of sol–gel auto-combustion and ultrasonic irradiation methods. In a typical procedure, a stoichiometric amount of metal nitrates (molar ratio of Co^{2+}: Fe^{3+} was 1:1) were dissolved in a certain amount of deionized water by stirring on a hotplate at 90 °C. Glycine was then added to the mixture solution to chelate metal ions. The molar ratio of glycine to metal ions used was 0.25:1.0. An ammonia solution was added to adjust the pH value to 9.5. The clear solution was refluxed 2 h at 100 °C to get complex in N_2 atmosphere. By increasing the temperature up to 200 °C, the clear solution was slowly evaporated and then the viscous gel was formed. Keep heating, the gel precursors were combusted to form the brown-colored loose powders. Finally, the as-burnt powders were calcined in air at 750 °C for 4 h with a heating rate of 10 °C/min to obtain cobalt ferrite nano-particles. Then, the product was placed in ultrasonic irradiation bath at 15 °C for 45 minutes.

3. Results and discussion

The experimental observations showed that gel with the molar ratio of 0.25:1.0 (nitrates: fuel), exhibit auto-catalytic combustion behavior. The temperature reached in the combustion reaction has an important effect on the crystallite size of the produced powder. By adjusting the glycine-to-nitrite ratio (G/N), the reaction temperature, can be controlled and thereby control the crystallite size of the resultant powder. When the gel was ignited, the combustion process rapidly propagated forward until all the gel was burnt out completely to form loose powder. Glycine is considered to serve as fuel for the combustion reaction, being oxidized by nitrate ions.

The effects of ultrasound radiation on chemical reactions are due to the very high temperatures and pressures that develop during the sonochemical cavity collapse by acoustic cavitation. With the action of ultrasonic cavitation, a high shear-rate is maintained throughout the solution, and the distance between particles can be sustained by the bubbles until the end of the reaction. In addition, the shock-wave that arisen by acoustic cavitation leads to strong shearing and fragmentation into particles, disrupting the aggregation between particles and control the size and size distribution. The surface activity of particles may also be restrained [23].

Fig. 1 shows XRD pattern of the nano-crystalline cobalt ferrite calcined at 750 °C for 4 h. It shows clearly that pure spinel ferrite was obtained when the stoichiometric molar ratio of Co and Fe was used. This sample is single phase ferrite ($CoFe_2O_4$) with cubic spinel structure (space group Fd3m) with a_0 = 8.380 Å. There are no detectable traces of extra crystalline or amorphous phase.

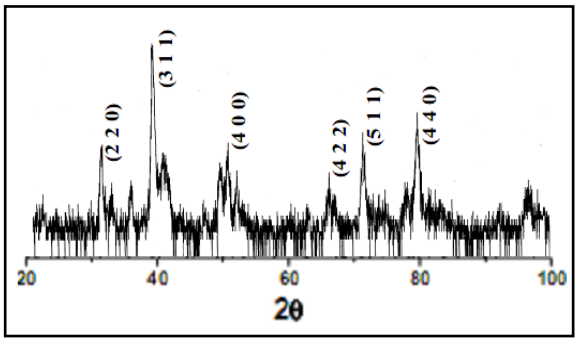

Fig. 1. XRD pattern of the nano-crystalline cobalt ferrite

The particle size of the synthesized cobalt ferrite samples estimated from X-ray peak broadening of the (3 1 1) peak using Scherrer equation:

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

where D is the particle size, λ is the wavelength of Cu Kα, β is the full width at half maxima (FWHM) of the diffraction peaks, and θ is the Bragg's angle in radian. The crystallite size for sample was 39.12 nm. Crystallite percent of $CoFe_2O_4$ phase was achieved 75.12 %. The resultant nano-scaled crystallite size of sample is due to two characteristics of the reaction system. One is that the reactants have been uniformly dispersed at an atomic or molecular level before reaction, so when ignition occurrs, the nucleation process can be completed through only the rearrangement and short-distance diffusion of nearby atoms. The other is that the rate of combustion reaction is so high that enough time and energy are not provided for the long-distance diffusion of atoms and obvious growth of the crystallites, as a result of which, the initial nano-phase is retained.

The SEM image (Fig. 2) of the Co-ferrite sample shows that the morphology of particles were almost spherically, regular in shape and dispersed uniformly, but agglomerated to some extent due to the interaction between magnetic nanoparticles, whereas the gel exhibits relatively porous network. The porous feature of agglomerates is attributed to the liberation of large amount of gas during combustion.

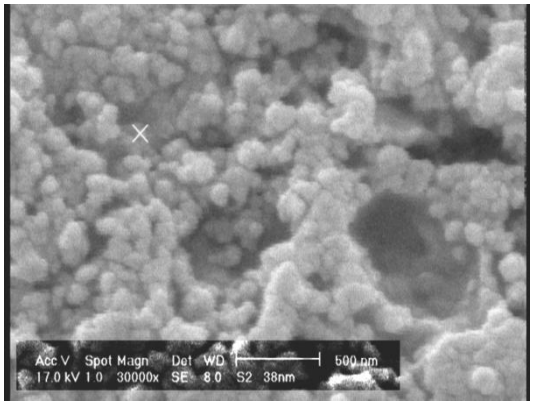

Fig. 2. The SEM image of the Co-ferrite sample.

The magnetization measurements for the as prepared cobalt ferrite were carried out using a vibrating sample magnetometer (VSM) at room temperature with an applied magnetic field of 10 kOe. The magnetic hysteretic loops of the $CoFe_2O_4$ are shown in Fig. 3, which indicates that the values of saturation magnetization (M_S) and coercivity (H_C) are 19.19 emu/g and 1171.5 Oe, respectively, which is lower than the values reported for $CoFe_2O_4$ bulk ferrite [24]. Although the coercive force is closely related to the microstructure as well as some other complex factors, it has been confirmed that the dimension of the magnetic crystallites exceeding the single domain critical size will cause a decrease in the coercive force for the appearance of multi-domain grains [25].

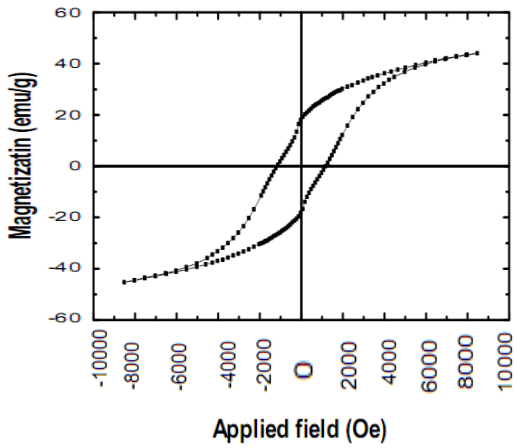

Fig. 3. The magnetic hysteretic loops of the $CoFe_2O_4$.

4. Conclusions

Nano-crystalline $CoFe_2O_4$ ferrites have been successfully synthesized by combination of sol–gel auto-combustion and ultrasonic irradiation methods. This synthesis process is an economical method for the preparation of ferrite nano-particles with respect to time and simplicity. X-ray diffraction analysis confirms the formation of a spinel phase. $CoFe_2O_4$ nanopowder with a moderate M_s and a relatively high H_c was obtained after sample was calcined at 750 °C for 4 h. In addition to the advantages of high-quality production, ease manipulation at low temperature and low cost, this method is open to conveniently doping other rare-earth ions with partially filled 4f orbits, which would provide a wider space for further improving the magnetic properties of $CoFe_2O_4$ nanocrystalline.

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