Magnetic properties comparison of $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles prepared by different methods

A. R. JELVANI, GH. R. AMIRI*, S. FATAHIAN, S. MANOUCHEHRI[a], M. HABIBI, R. MOUSAREZAEI DEHAGHI
Falavarjan Branch, Islamic Azad University, Isfahan, Iran
[a]*Department of Physics, Malek-Ashtar University of Technology, Shahinshahr, Esfahan, Iran.*

$Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles with diameters less than 11 nm were prepared by three different methods of microwave, co-precipitation and Low Temperature Solid State Reaction (LTSSR). Magnetic and structure properties of the products were investigated by X-Ray Diffraction (XRD), Alternating Gradient-Force Magnetometer (AGFM) and Transmission Electron Microscopy (TEM). Magnetic properties of samples depended on the synthesis method. The X-ray analysis shows the samples have spinel phase. The Curie temperatures of the samples were measured and they were lower than the bulk ones. In addition, all of $Co_{0.5}Zn_{0.5}Fe_2O_4$ samples exhibit a small hysteresis loop at room temperature.

(Received October 18, 2011; accepted November 23, 2011)

Keywords: Nano crystallite, Magnetic properties, Ferrite nanoparticle

1. Introduction

Magnetic nanoparticles have some important industrial applications such as ferro-fluids, magnetic drug delivery, high-density information storage and in medicine for the treatment of various type of cancers [1,2]. The composition of ferrospinels can be described by the general formula $M^{2+}[Fe^{3+}Fe^{3+}]O_4$, which has wide applications in both the technological and the catalytic fields [3,4].

In the spinel oxide ferrite ($Me_{II}Fe_2O_4$) nanoparticles, the cation distribution between the tetrahedral (A) and octahedral (B) sites affects on the spin alignment and the degree of spin-canting. The cation distribution can be size dependent and may also depend on the synthesis method [5].

Curi temperature is one of the most remarkable parameters of every ferrite. It is an intrinsic characteristic of the spinel ferrites which can be controlled by preparation conditions and substitution of different Curi temperature Tc of 530 °C [5].

Magnetic nanoparticles can be synthesized by different methods such as co-precipitation, Low Temperature Solid State Reaction (LTSSR), wetted chemical method, ball mill, microwave and sol-gel. Magnetic properties of nanoparticles are strongly depend on the synthesize method because variation in size distribution is depend on the synthesize method. In this essay an attempt is to comparison the magnetic properties of $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles which are produced by three methods of microwave, co-precipitation and LTSSR.

2. Experimental

2.1. Synthesis of $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles by microwave method

For this purpose, the solution of cobalt chloride, zinc chloride and iron chloride (all from Merck company) by the weight ratio of 1:1:4, was prepared in the ethylene glycol (EG), under vigorous stirring. Also, the NaOH solution was prepared in Double-distilled water. The NaOH solution was poured into the other solution and they were put into the Microwave oven. Then the microwave was set for the fish cooking and was turned on for 10 minutes. After that, very thick smoke was raised from the sample and the sample was ignited and Remains soft powder. The powder was washed several times by distilled water and was dried at room temperature.

One of the most important aspects of the microwave heating is that it utilizes the inherent properties of the liquids, solids and their mixtures to transform microwave energy into heat that promotes the reactions. EG is one of the best microwave absorbing agents due to its high ionic conductivity, thus leading to a high heating rate and a significantly shortened reaction time (10 min). Simultaneously, the temperature of the reaction can be reached up to 190 °C under microwave heating. This leads to the high crystallinity of the products. (Attention that the EG boiling point is about 195 °C) [6].

2.2. Synthesis of $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles by Co-Precipitation method

$Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles were synthesized using chemical co-precipitation method, without subsequent calcinations steps. For this purpose, four solutions of $CoCl_2$ (0.05 M), $ZnCl_2$ (0.05 M), $FeCl_3$ (0.2 M) and NaOH

(0.8 M) (all from Merck company) were prepared in the distilled deionized water, under vigorous stirring. At first, the NaOH solution was stirred constantly and heated to 353 °K. Then the solutions of cobalt, zinc and ferric chlorides were mixed. The composition were heated to 353 °K and added to NaOH solution. The mixed solutions were kept temperature 353 °K for 1 houre, under vigorous stirring. The pH of the mixture was around 12 because of the presence of NaOH. The precipitate is isolated from the solution by several times filtration and washing by deionized distilled water, and dried at room temperature.

2.3. Synthesis of $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles by LTSSR method

The chemical reagents are ferric chloride ($FeCl_3.6H_2O$), cobalt chloride ($CoCl_2.6H_2O$), zinc chloride ($ZnCl_2$) and sodium hydroxide (NaOH), which provided with high purities from Merck. To get $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles, powders of $ZnCl_2$, $CoCl_2$, $FeCl_3$ and NaOH were mixed in their stoichiometric ratios (1:1:4:16). The mixture was milled at room temperature for 30 minutes. After that the powder were washed with distilled water several times.

To obtain nanoparticles with formula $Co_{0.5}Zn_{0.5}Fe_2O_4$ the following reaction can be written:

$$(0.5ZnCl_2 + 0.5CoCl_2) + 2FeCl_3 + 8NaOH \rightarrow Co_{0.5}Zn_{0.5}Fe_2O_4 + 4H_2O + 8NaCl$$

The X-ray diffraction(XRD) pattern of the samples were obtained by a diffractometer, (BRUKER, D8 model), using Cu-Kα radiation (λ=1.5406 Å). Average crystallite sizes of the powders were calculated by the Scherrer's formula:

$$D=0.9\lambda/B\cos\theta,$$

Where D is mean crystallite size, θ is the Bragg angle and B is the broadening of the diffraction peaks, measured at half their maximum intensities, due purely to crystallite size.

The room temperature hysteresis loop of the samples was obtained by Alternating Gradient-Force Magnetometer (AGFM) up to 10000 Oe. The Curie temperature was determined by faraday balance equipment.

3. Results and discussion

Fig. 1 demonstrates the XRD patterns of the $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles which are synthesized by three methods. It can be seen that, all the samples have single phase and also have the ferrite spinel structure. The mean size of the particles was determined by Debye-Scherer formula. The results are shown in Table 1.

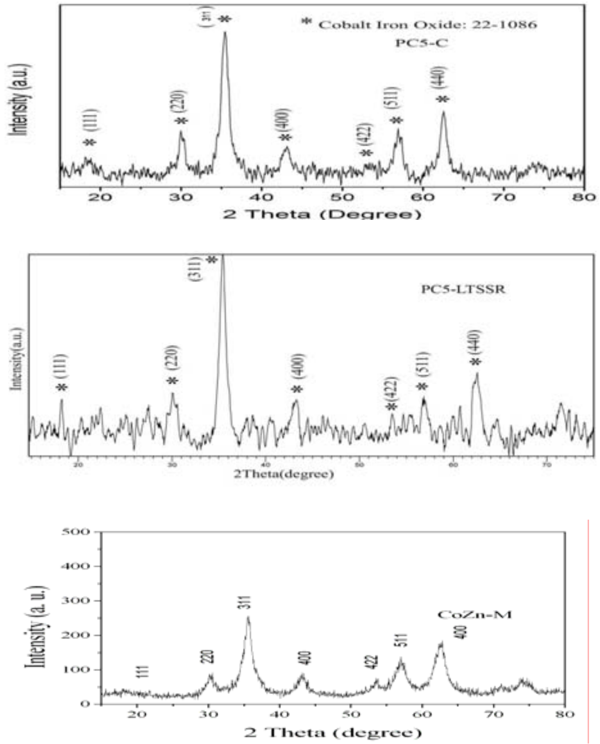

Fig. 1. XRD patterns of the $Co_{0.5}Zn_{0.5}Fe_2O_4$ samples a) co precipitation method, b) LTSSR method c) Microwave method.

Fig. 2 illustrates the TEM photographs of the sample which is synthesized by co-precipitation method. As can be seen a fine size distribution was obtained. The size was determined 10 nm that have a good agreement with XRD results.

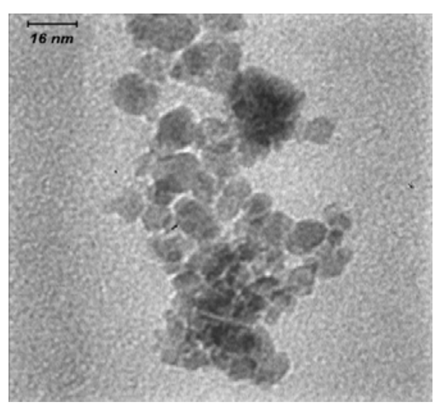

Fig. 2. TEM photograph of the $Co_{0.5}Zn_{0.5}Fe_2O_4$ samples which are synthesized by co precipitation method (size of nanoparticles 10 nm).

Fig. 3 indicates the AGFM curve of the $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles which are synthesized by three methods. As can be seen, all samples cannot reach a saturation state in the presence of a relatively strong magnetic field of even 10000 Oe. The saturation magnetization was determined by extrapolation of magnetization curve on the basis of $1/H$ when $1/H \to 0$. The dependence of the coercivity field (Hc) and Ms on the Co-Zn substitution is shown in Table 1. Ms of samples is smaller than that of the bulk sample with the same composition. The decrease in saturation magnetization is due to decrease in particle size and surface spin effects of small particles that the formations a surface layer in which magnetic moment do not contribute to the magnetization in the applied field [7].

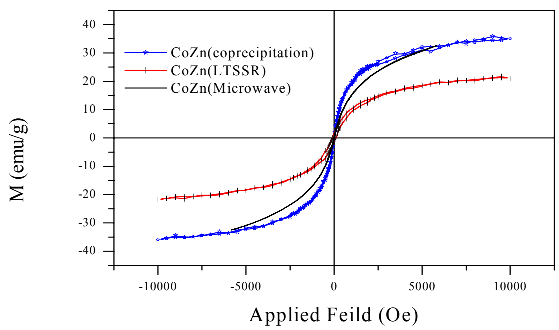

Fig. 3. AGFM curves of $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles.

The magnetization temperature dependency for all samples is shown in Fig. 4. The Curie temperatures (Tc) were determined when the relative magnetization less than 0.5 percent and listed in Table 1. The Curie temperature is smaller than the bulk ones. It is due to the variation of the crystallite size.

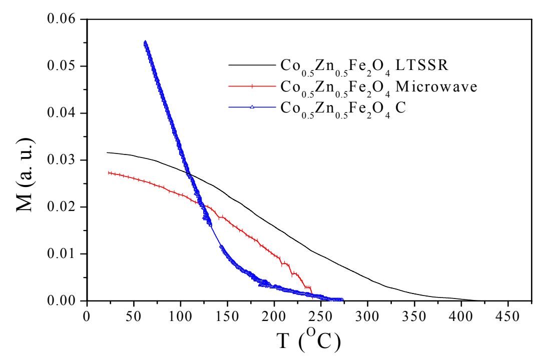

Fig. 4. The magnetization temperature dependency for all samples.

Table 1. The physical properties of the samples $Co_{0.5}Zn_{0.5}Fe_2O_4$.

Synthesis Method	M (emu/g) 10kOe	Mr(emu/g)	H_C(Oe)	T_C(^{0}C)	D(nm) XRD	D(nm) TEM
Microwave	33	0.6	21	244	6	-
Co-Precipitation	35.5	0	0	201	9	10
LTSSR	22	1.3	100	369	11	-

4. Conclusions

Nanocrystallite powders of $Co_{0.5}Zn_{0.5}Fe_2O_4$ were synthesized by three methods. There are changes in many physical and magnetically properties. It can be concluded that, the Curie temperature, saturation magnetization, Mr and H_c are all depend on nanocrystallite size and method.

Acknowledgements

This study was completed at Islamic Azad University, Falavarjan Branch, and supported by the Graduate Studies Office.

References

[1] G. Nedelcu, Digest Journal of Nanomaterials and Biostructures, **3**(2), 99 (2008).
[2] Gh. R. Amiri, M. H. Yousefi, M. R. Aboulhassani, M. H. Keshavarz, D. Shahbazi, S. Fatahian, M. Alahi, Digest Journal of Nanomaterials and Biostructures, **5**(3), 1025(2010).
[3] K. Sreekumar, T. Raja, B. Kiran, S. Sugunan, B. Rao, Appl Catal A; **182,** 327 (1999).
[4] S. Fatahian, D. Shahbazi, M. Pouladian, M. H. Yousefi, Gh. R. Amiri, Z. Shahi, H. Jahanbakhsh, Digest Journal of Nanomaterials and Biostructures, **6**(3), 1161 (2011).
[5] M. H. Yousefi, S. Manouchehri, A. Arab, M. Mozaffari, Gh. R. Amiri, J. Amighian, Materials Research Bulletin, **45**, 1792 (2010).
[6] W. W. Wang, Journal of Materials chemistry and Physics, **108**, 227 (2008).
[7] R. H. Kodama, A. E. Berkowitz, Phys Rev B **59**, 6321 (1999).

*Corresponding author: amiri@iaufala.ac.ir