Magnetic properties of $CoFe_2O_4$ and $Co_{0.5}$ $Zn_{0.5}Fe_2O_4$ ferrite nanoparticles synthesized by microwave method

GH. R. AMIRI*, S. FATAHIAN, A. R. JELVANI, R. MOUSAREZAEI DEHAGHI, M. HABIBI
Falavarjan Branch, Islamic Azad University, Isfahan, Iran

$CoFe_2O_4$ and $Co_{0.5}$ $Zn_{0.5}Fe_2O_4$ nanoparticles from 4 to 27 nm were produced by microwave method. The products were characterized by X-Ray Diffraction (XRD) and magnetic properties measurements such as Alternating Gradient-Force Magnetometer (AGFM). The X-ray analysis shows that the samples have spinel phase. The saturation magnetization was disagreement with the bulk ones. The Curie temperatures of the samples were lower than the bulk ones. The curie temperature of $Co_{0.5}$ $Zn_{0.5}Fe_2O_4$ was 244 °C and for $CoFe_2O_4$ was 450 °C. It seems this is due to the presence of Zn^{+2} ion in the spinel structure of $Co_{0.5}$ $Zn_{0.5}Fe_2O_4$.

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1. Introduction

Magnetic nanoparticles have many important applications in different fields like medicine, industry and military. There is an increasing interest in producing of new magnetic nanoparticles because of their wide applications [1-4].

Since the spinel ferrites crystallize in a FCC lattice with eight formula units in cubic unit cell, they can be distinguished as two basic types, normal and inverse spinels [5]. The composition (M) of ferrospinels that can be described by the general formula of spinels is $M_{2+}[Fe_{3+}Fe_{3+}]O_4$, that has wide applications in both technological and catalytic fields [6-8].

However, unusual distribution of cations among the tetrahedral (T) and octahedral (O) sites of the coordinated oxygen is an important factor for the explanation of catalytic effectiveness [8, 9]. Since the major influence of the activity comes from the O-ions, probably for the presence of large exposure of these ions on the surface, it enables spinels to withstand even in extremely reducing conditions [10].

We have prepared Co Fe_2O_4 and $Co_{0.5}$ $Zn_{0.5}Fe_2O_4$ ferrites using microwave method. with the average crystallite sizes ranging from 4 to 27 nm. The magnetic nanocrystallites were characterized with an emphasis on determination of saturation magnetization and Curie temperature.

2. Experimental

2.1. Synthesis of $CoFe_2O_4$ nanoparticles by microwave method

For this purpose, the solution of cobalt chloride and iron chloride (both from Merck company) by the weight ratio of 1:2, 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. To obtain the nanoparticles with formula Co Fe_2O_4 the following reaction can be written:

$$CoCl_2 + 2FeCl_3 + 8NaOH \rightarrow CoFe_2O_4 + 4H_2O + 8NaCl$$

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) [11].

The five specimens of the $CoFe_2O_4$ ferrites were synthesized and annealed for 2h but in different temperatures. The samples were named by their annealing temperature. Therefore, the sample which was annealed at 30 °C was named Co30, 500 °C (Co500), 800 °C (Co800), 1000 °C (Co1000) and 1200 °C (Co1200).

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

In order to obtain $Co_{0.5}$ $Zn_{0.5}Fe_2O_4$, 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. To obtain the 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 four specimens of the $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrites were synthesized and annealed for 2h but in different temperatures. The samples were named by their annealing temperature. Therefore, the sample which was annealed at 30 ^{o}C was named CoZn30, 500 ^{o}C (CoZn500), 800 ^{o}C (CoZn800) and 1000 ^{o}C (CoZn1000).

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). The Average crystallite powder sizes were calculated by the Scherrer's formula:

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

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

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

XRD patterns for $CoFe_2O_4$ and $Co_{0.5}\,Zn_{0.5}Fe_2O_4$ at different temperatures were shown in Fig. 1 and Fig. 2. As can be seen, the samples Co30, Co500, Co800, Co1200, CoZn30, CoZn 500, CoZn 800 and CoZn 1000 have spinel structures, while for the sample of Co1000 the miner Hematite phase was also observed.

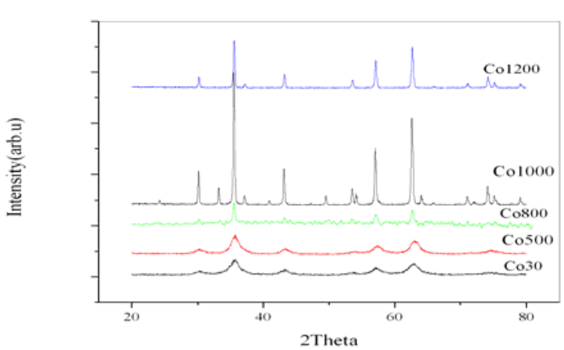

Fig. 1. X-ray diffractogram of $CoFe_2O_4$ for different temperatures.

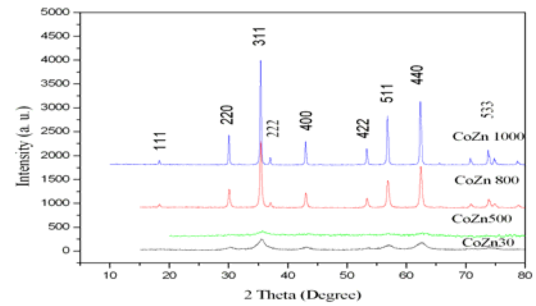

Fig. 2. X-ray diffractogram of $Co_{0.5}\,Zn_{0.5}Fe_2O_4$ for different temperatures.

The average crystallite sizes for all of $CoFe_2O_4$ and $Co_{0.5}\,Zn_{0.5}Fe_2O_4$ powders, calculated by Scherrer`s formula, were found within 4 to 27.0 nm and listed in Table 1.

Also it can be seen, the smallest size of nanoparticles obtained for the samples annealed at room temperature (Co30, CoZn30) and the size increased with increasing the annealing temperature.

AGFM measurements for the samples are given in Fig. 3 and Fig. 4, and the values of the magnetic parameters at room temperature listed in Table 1. These physical properties are related to the size increment by increasing annealing temperatures.

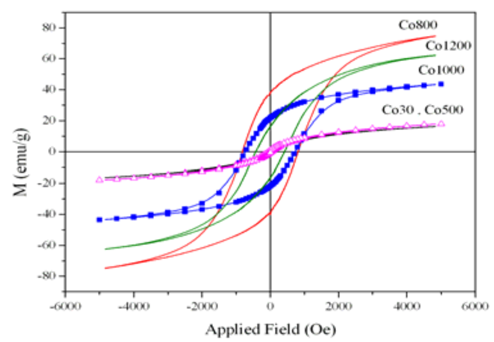

Fig. 3. AGFM Plot of magnetization versus applied field for $CoFe_2O_4$ samples.

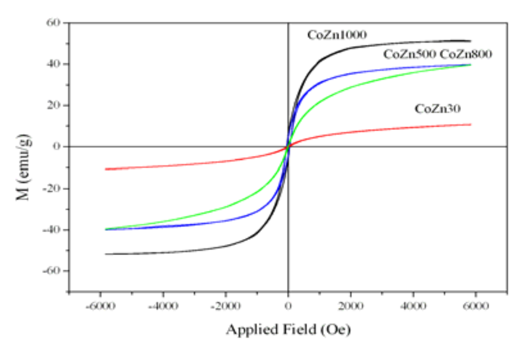

Fig. 4. AGFM Plot of magnetization versus applied field for $Co_{0.5}Zn_{0.5}Fe_2O_4$ samples.

The temperature dependent magnetization for Co30 and CoZn30 are shown in Fig. 5 and Fig. 6. They are also listed in Table 1. The Curie temperature is smaller than the bulk ones. It can be due to crystallite size dependent.

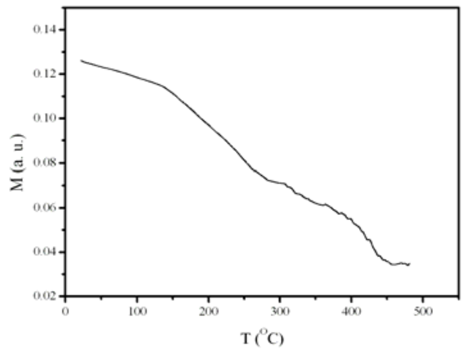

Fig. 5. The temperature dependent magnetization for Co30 sample.

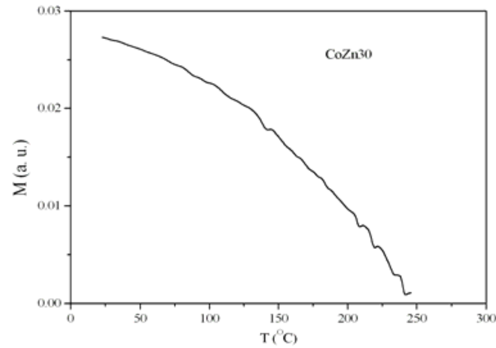

Fig. 6. The temperature dependent magnetization for CoZn30 sample.

Table 1. The physical properties of the samples.

sample	M (emu/g) 10kOe	Mr(emu/g)	H_C(Oe)	T_C(^{0}C)	(nm) XRD
Co30	15	0.12	10	450	4.1
Co500	16.4	0.71	39.5	----	8
Co800	74.2	36.9	812	----	20.8
Co1000	43	21.7	722	-----	26.8
Co1200	62.5	16.1	432	-----	26.8
CoZn30	10.7	0.13	12	244	7.3
CoZn500	40	0.5	12	----	11
CoZn800	40	4.6	44	----	26.2
CoZn1000	51.16	3.8	50.5	-----	33.9

4. Conclusion

Obviously, one of the simplest methods for synthesized powder of ferrite is microwave method, so this has been used to produce the nanostructure $CoFe_2O_4$ and $Co_{0.5}$ $Zn_{0.5}Fe_2O_4$. The selected important point is the effect of temperature variations on the formation desirable phase, size distribution, magnetic field (Ms 15 emu/g at 30 °C, while it reaches 74.2 emu/g at 800 °C in $CoFe_2O_4$, but in $Co_{0.5}$ $Zn_{0.5}Fe_2O_4$ at 30 °C 10.7 emu/g, it will be increased up to 51.16 emu/g at 1000 °C and Hc at 800 °C is 812 Oe for $CoFe_2O_4$, while at 1000 °C for $Co_{0.5}$ $Zn_{0.5}Fe_2O_4$ becomes 50.5 Oe). The Curie temperature is smaller than the bulk ones. It can be due to crystallite size dependent and the presence of Zn ion.

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*Corresponding author: amiri@iaufala.ac.ir