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Structural and Magnetic Properties of Co0.5Ni0.5-xMnxFe2O4(x=0, 0.15, 0.25, 0.35, 0.5) Ferrite Nanoparticles Prepared via Sol-Gel Auto-Combustion Method

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ABSTRACT

In this study, $Co_{0.5}Ni_{0.5-x}Mn_xFe_2O_4$ (x=0, 0.15, 0.25, 0.35, 0.5) ferrite nanoparticles were prepared by sol-gel auto-combustion method. Structural, magnetic and morphology properties of obtained nanoparticles were investigated with X-ray Diffraction (XRD), Vibrating Sample Magnetometer (VSM) and Transmission Electron Microscopy(TEM), respectively. The XRD results show that the most dominant peaks for samples is related to the Spinel phase. Crystalline size using Scherrer's equation for different values of x were obtained between 44 to 64 nm. VSM results showed that the saturation magnetization and coercivity values changed with increasing Mn. TEM images obtained results are in good agreement with the XRD results.

Keywords

Sol–gel process; Magnetic hysteresis; Coercivity; X-ray diffraction.

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1. INTRODUCTION

Soft ferrites with formula MFe_2O_4 are a class of magnetic materials with spinel structure which have outstanding properties such as extreme electrical resistivity, high permeability and low hysteresis losses. These features make them useful in numerous applications like high-frequency devices, microwave components, data storing and retrieving components, sensors, targeted drug delivery, transformer cores and magnetic fluid[1-2].

Various methods are used for constructing ferrite nanoparticles. Some of these methods are sol-gel technique, the co-precipitation, hydro thermal and mechanical methods. Among these, the sol-gel method is one of the most convenient methods for making nanoparticles because it yields homogeneous product of high purity with relatively low calcination temperature and time [3-4].

Cobalt ferrite is a famous hard magnetic material with high crystalline coactivity and anisotropy and an average magnetization which is used in high-density magnetic recording disks [5]. Nickel ferrite is a soft and common magnetic material with anisotropy and magneto crystalline lower than cobalt ferrite and can be used in sensors. An effective way to decrease the isotropy of cobalt ferrite is the substitution of Co^{2+}ions for Ni^{2+}ions [6]. Adding manganese to cobalt ferrite can lead to improvement in properties of contraction sensors [7].

In a recent study, the effect of substitution of manganese for iron in cobalt ferrite has been investigated. The result has demonstrated that with increasing the amount of manganese, magnetization and Curie temperature have declined [8].

In another study the effect of substitution of manganese for iron in $CoFe_{2-x}Mn_xO_4$ ferrite has been investigated. Results shown that for x=0.1, magnetization increased and then decreased for the larger values of x [9].

In this work, the effect of substitution of manganese for nickel in $Co_{0.5}Ni_{0.5-x}Mn_xFe_2O_4$ (x=0, 0.15, 0.25, 0.35, 0.5) nanoferrite on structural, morphological and magnetic characteristics of nanoparticles have been investigated. We expect with regard to the difference in ion radius and magnetic moment of manganese compared with other ions in the sample, interesting properties emerge.

2. EXPERIMENTDETAILS

$Co_{0.5}Ni_{0.5-x}Mn_xFe_2O_4$ (x=0, 0.15, 0.25, 0.35, 0.5) ferrite nanoparticles prepared via sol-gel auto-combustion method. For this purpose, iron nitrates, cobalt, manganese and nickel as inorganic reactants, citric acid as the complexing agent and distilled water as the solvent were used. Synthesis technique for nanoparticles is as follows: First, Iron nitrate along with cations of other metal nitrates dissolved in distilled water with a molar ratio of 2:1.Then citric acid added to the solution with a molar ratio 3 times the total moles of metal nitrates. After that the pH value was fixed at 7 using ammonium hydroxide. The resulted solution was stirred for one hour at room temperature leading to the formation of a homogeneous and stable sol. This sol was slowly heated at a temperature of 80 °C in order to evaporate the solvent until obtaining a viscous gel. Then the gel was placed in the oven at 250 °C so the combustion process took place. After combustion, the burnt gel was heated for 2 hours in an oven to dry out completely. Finally, the dried gel was removed from the oven and pulverized in a mortar and pestle to obtain a finely homogeneous powder. Resulted powders were calcinated for 5 hours at 700 °C till finally ferrite nanoparticles were obtained.

To investigate structural characteristics of the samples X-ray diffraction analysis (model: Bruker with Cu tube and 1.5406 Å of wave length) was used. The morphology of the sample was studied with the help of a transmission electron microscope (model:900Em Zeiss). To study the magnetic properties of the samples a Vibrating Sample Magnetometer (VSM) (model: Lake Shore model no. 7400) was used.

3. RESULTSAND DISCUSSION

3.1. X-ray diffraction

X-ray diffraction pattern of $Co_{0.5}Ni_{0.5-x}Mn_xFe_2O_4$ (x =0, 0.15, 0.25, 0.35, 0.5) nanoparticles is shown in Figure 1. As can be seen, the sample shave cubic spinel structure and most of the peaks are related to the spinel phase.

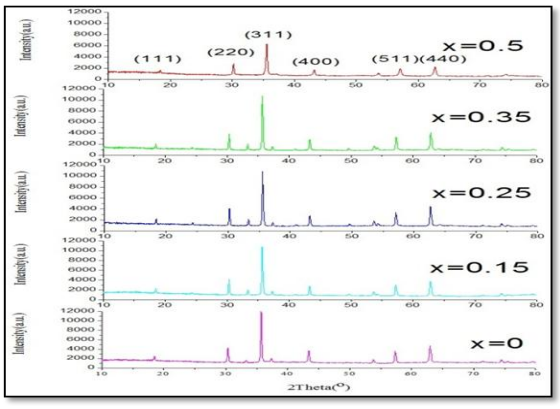

Figure 1: X-ray diffraction pattern of $Co_{0.5}Ni_{0.5-x}Mn_xFe_2O_4$ (x=0, 0.15, 0.25, 0.35, 0.5)ferrites

Crystallite size was calculated with the help of the Scherrer equation considering the wide of diffraction peak (311) which has the maximum intensity:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

(1)

Where D is the crystallite size, β is the peak wide that half maximum height (calculated using XRD data utilizing the Xpert Plus software), λ is the wavelength of X-ray and k is the Scherrer constant (~ 0.9).

The following equation was used to calculate the lattice parameter:

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \quad (2)$$

In this relation d_{hkl} is the distance between (hkl) planes.

X-ray density was calculated using the following equation:

$$\rho_x = \frac{8M}{N_a a^3} \quad (3)$$

Where M is the molar mass, N_a is the Avogadro's number and a^3 is the unit cell volume. Number 8 in the numerator is the number of molecules per unit cell of cubic spinel structure.
Lattice parameter, X-ray density and the size of crystallite grains are given in Table1.

Table 1: Crystallite size, lattice constant and X-ray density for different x

Name of the sample	Crystallite size (nm)	Lattice constant (Å)	Calcination temperature (°C)	X-ray density (g/cm^3)
$Co_{0.5}Ni_{0.5}Fe_2O_4$	63.72	8.33	700	5.39
$Co_{0.5}Ni_{0.35}Mn_{0.15}Fe_2O_4$	52.11	8.34	700	5.36
$Co_{0.5}Ni_{0.25}Mn_{0.25}Fe_2O_4$	63.71	8.37	700	5.29
$Co_{0.5}Ni_{0.15}Mn_{0.35}Fe_2O_4$	52.10	8.35	700	5.32
$Co_{0.5}Mn_{0.5}Fe_2O_4$	44.30	8.37	700	5.27

As can be seen the size of the crystallites in the samples are between 44 to 64 nm. It is almost constant and increases in hundredths in most cases. This can happen because of the substitution of Mn ion with 0.83 Å in radius for Ni ion with a radius of 0.74 Å [10]. However, there is a decrease in the lattice constant in one case which can be due to the displacement of larger ions with smaller ones between A and B positions. This chance would be greater considering the obtained results from the magnetic measurements. Increasing the amount of Mn reduces the X-ray density for all samples except for x=0.35.

3.2. Magnetic properties

Hysteresis curves of samples $Co_{0.5}Ni_{0.5-x}Mn_xFe_2O_4$ (x =0, 0.15, 0.25, 0.35, 0.5) which are calcinated at 700°Cobtained using the vibrating sample magnetometer (VSM) are shown in Figure 2.

As can be seen in Figure 2 and Table 2, the saturation magnetization of the samples$Co_{0.5}Ni_{0.5-x}Mn_xFe_2O_4$ (x =0, 0.15, 0.25, 0.35, 0.5) shows first of all a decrease, then an increase and a decrease subsequently. The increase can be due to the substitution of Mn ions with a magnetic moment of 5 Bohr Magneton for Ni ions with a magnetic moment of 2 Bohr Magneton at the position B. The decrease can be due to the substitution of Mn ions with a magnetic moment of5 Bohr Magneton for Ni ions with a magnetic moment of 2 Bohr Magneton at the position A [11-12].

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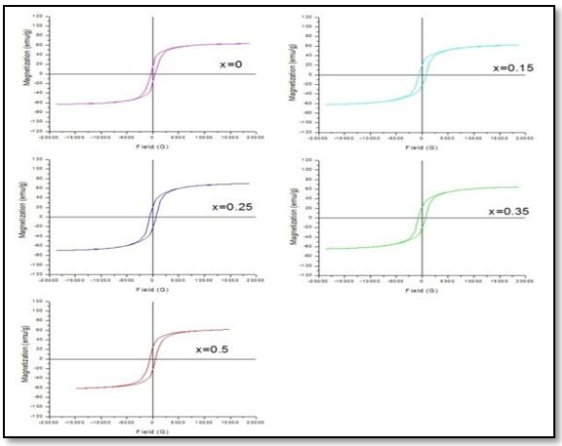

Figure 2: Magnetic Hysteresis loop of $Co_{0.5}Ni_{0.5-x}Mn_xFe_2O_4$ (x=0, 0.15, 0.25, 0.35, 0.5) ferrites

Magnetic anisotropy constant was calculated by the following equation:

$$H_c = \frac{0.96\,K}{M_s} \quad (4)$$

Where K is the constant of anisotropy.

As can be seen in Table 2 H_c and K decrease in some of the samples and increase in others which with the consideration of high anisotropy of cobalt the increase can be due to the ion transfer from the position A to the position B and the decrease can be due to the transfer of cobalt ion from the position B to the position A in accordance with the results in table 2 for M_s.

Table 2: Magnetic properties of $Co_{0.5}Ni_{0.5-x}Mn_xFe_2O_4$

X	K(erg/gm)	H_c(Oe)	M_s(emu/g)	Calcination temperature (°c)
0	26277.54	398.9	63.24	700
0.15	45505.78	705.63	61.91	700
0.25	44823.01	617.45	69.69	700
0.35	45678.95	681.38	64.37	700
0.5	37938.78	592.89	61.43	700

3.3. Morphology characterization

For a detailed study of the size distribution of nanoparticles a TEM image, shown in Figure 3, is taken from the $Co_{0.5}Mn_{0.5}Fe_2O_4$ samples calcined at 700 ° C. Considering the form of the nanoparticles, this sample has been quasi-spherical and the particle distribution is uniform. Grain size has been smaller than 60 nm, which is in good agreement with XRD results. However, in some areas, there is little accumulation.

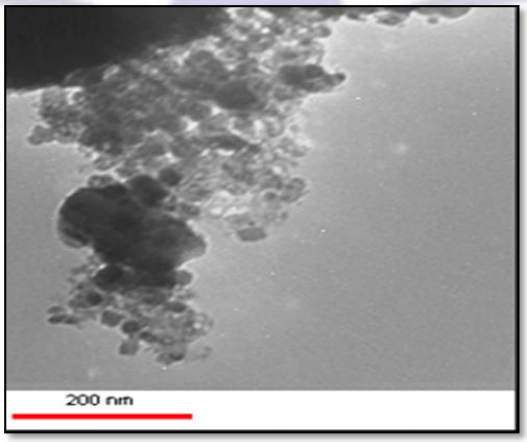

Figure 3: TEM image of $Co_{0.5}Mn_{0.5}Fe_2O_4$ sample

4. CONCLUSION

In this study, the effect of the substitution of Mn atoms for Ni in $Co_{0.5}Ni_{0.5-x}Mn_xFe_2O_4$ (x =0, 0.15, 0.25, 0.35, 0.5) ferrite on structural, magnetic and morphological characteristics of the samples has been investigated. The XRD results confirm the formation of the spinel phase for all samples. Magnetic characterization of the samples shows that with the substitution of Mn for Ni in cobalt-nickel ferrite, saturation magnetization and coercivity of the samples changes from 61 to 70(emu/g) and from 399 to 706 (Oe) respectively. Considering these features they are more suitable for utilizing in magnetic recording devices. TEM results are in good agreement with the XRD results.

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Author’ biography

Dr. Ahmad Amirabadizadeh with Iranian nationality was born in 1964 in Bojnord, Iran. He received BSc in 1988 (University of Birjand, Iran), M.Phil in 1995 (Qaud-e-Azam University, Islamabad, Pakistan) and Ph.D in 2003 (ferdowsi University of Mashhad, Iran) on solid State Physics. From 2004 to date, he has been teaching Physics in University of Birjand as asst. Proff. in physics department. From 2012 to date, he was head of Magnetism and Superconductivity lab based in University of Birjand. Upto now, about 20 Master students have finished their thesises on Superconductivity ond nanomagnetiam with him and his pubished articles in international journals are more than 20.