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Effect of zinc concentration on the magnetic properties of cobalt–zinc nanoferrite

Ritu Rani [a,*], S.K. Sharma [a,b], K.R. Pirota [b], M. Knobel [b], Sangeeta Thakur [a], M. Singh [a]

[a] *Department of Physics, Himachal Pradesh University, Shimla 5, India*

[b] *Instituto de Fisica GlebWataghin, Universidade Estadual de Campinas (UNICAMP), Campinas 13.083-859, SP, Brazil*

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Abstract

Nano-cobalt–zinc ferrite (CZFO) $Co_{(1-x)}Zn_xFe_2O_4$ with varied quantities of zinc ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) have been prepared by solution combustion method. X-ray diffraction and transmission electron microscopy confirmed the size, structure and morphology of the nanoferrites. The addition of zinc in cobalt ferrite has been shown to play a crucial role in enhancing the magnetic properties. Ferromagnetic ordering is observed in nano samples at room temperature. Zn substitution shows maximum saturation magnetization for $x = 0.1$, that is 56.74 emu/g and then decreases for further increase in Zn substitution. The dependence of Mössbauer parameters viz. isomer shift and hyperfine magnetic field with zinc concentration has been studied. Mössbauer results are also supported by magnetization data. The results obtained from this method make these samples suitable for preparing high quality nanocrystalline ferrite for high density data storage applications.

Keywords: Cobalt–zinc; Mössbauer spectra; Solution combustion method; X-ray diffraction; Saturation magnetization

1. Introduction

Nanoferrites are very important magnetic materials. These possess good magnetic properties along with very high d.c. resistivity. Among various magnetic materials, ferrites are the best in high frequency circuits. Interest in nano sized spinel ferrites has greatly increased in the past few years due to their importance in understanding the fundamentals in nano magnetism.

High magnetocrystalline anisotropy and good chemical stability has made cobalt ferrite ($CoFe_2O_4$) a very promising candidate for diverse applications as in magnetic drug delivery to magnetic recording applications such as audio and video tape and high density digital recording discs [1]. The magnetic properties of the $CoFe_2O_4$ are greatly affected by the size of the particles [2] and by cation substitution. These can be modified by a suitable composition and variation, e.g. by partial replacement of the Co ions by non magnetic Zn cation [3]. According to recent research Zn^{2+} substituted $CoFe_2O_4$ nanoferrite ($Co_{(1-x)}$–$Zn_xFe_2O_4$) exhibited improved magnetic and electrical properties [4–8]. Substitution of Co^{2+} with Zn^{2+} leads to introduction of non magnetic Zn^{2+} ions into A sites, thus increasing saturation magnetization, Ms leading to an increased magnetization [9].

A large number of methods has been developed to prepare $Co_{(1-x)}$–$Zn_xFe_2O_4$ nanoferrite, such as the co-precipitation [10], ceramic technique [11], forced hydrolysis [12], microwave combustion method [13], sol–gel method [14], solvothermal method [15], the standard solid-state reaction technique [16], and the PEG-assisted hydrothermal method [17]. Among them we have chosen combustion method for the preparation of nanoferrite, because the complex processes, expensive precursors, and low production rates are common problems [13]. There are very few reports on the $Co_{(1-x)}$–$Zn_xFe_2O_4$ nanoferrite prepared by combustion method. Therefore, aim of the present work is to study structural, Mössbauer and Magnetic properties of Co–Zn nanoferrite synthesized by solution combustion method. We have taken CZFO ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) as basic system for the following reasons. This sample is a mixture of $CoFe_2O_4$ with long range ferromagnetic transition temperature at 790 K and $ZnFe_2O_4$ with antiferromagnetic Neel temperature at 9 K. It has been reported that $CoFe_2O_4$ has the

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* Corresponding author. Tel.: +91 9418692500.
E-mail address: rituphysics@gmail.com (R. Rani).

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highest anisotropy constant among the ferrite spinels due to the presence of Co^{2+} ions on B sites. $CoFe_2O_4$ is a good candidate for magnetic recording media and magnetic fluids whereas; $ZnFe_2O_4$ is used as catalyst [13,18,19].

2. Experimental

CZFO nanoferrite with varied quantities of Zn ($x = 0.0$, 0.1, 0.2, 0.3, 0.4) were synthesized via solution combustion technique. The chemical reagents used in this work were ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$), and urea ($CO(NH_2)_2$) as a fuel. All reagents were of analytical grade and used without further purification. In a stoichiometric ratio Fe $(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and $CO(NH_2)_2$ in 1:1 ratio were mixed to obtain precursor solutions. This ratio is required for complete combustion of all materials. The precursor solution was prepared in distilled water by mixing stoichiometric amount of metal nitrates and urea. The obtained precursor solution then heated on a hot plate up to drying of the solution with evolution of large amount of gases (N_2O and CO_2) and then the solution starts to burn with release of lots of heat. The whole procedure takes place for minimum 2–3 h. The obtained powder samples were annealed at 500 °C for 4 h.

X-ray powder diffraction analysis was conducted on XPERT-PRO Diffractometer (XRD) using Cu Kα radiation. The patterns were recorded in 2θ range of 15–80° at room temperature. The phase structure of nanoferrites was analyzed by XRD. TEM was used to analyze the morphology of prepared nanoferrite samples. Mössbauer spectra were also studied at room temperature. The Mössbauer spectra were recorded using a conventional constant acceleration Mössbauer spectrometer with ^{57}Co in a Rh matrix as the Mössbauer source. Mössbauer spectra were analyzed by NORMOS (DIST) fitting. Magnetic measurements were obtained from a super conducting quantum interference device (SQUID) at room temperature (300 K).

3. Results and discussions

3.1. Structural analysis

The X-ray patterns of the synthesized CZFO nanoferrites ($x = 0.0$, 0.1, 0.2, 0.3, 0.4) are shown in Fig. 1. XRD patterns of all the samples show a typical cubic spinel structure. The crystallite size of the nanocrystalline samples was calculated using Scherrer formula [20]. To calculate the crystallite sizes from the Scherrer equation the full width at half maximum of the strongest reflection was used [21].

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

where D is the crystallite size, k is the Shape function for which a value of 0.9 is used. β is the full width at half maximum (FWHM) of the (3 1 1) peak, λ is the X-ray wavelength, and θ is the diffraction angle [22]. The broad peaks indicate that the mean crystallite size of the prepared samples CZFO ($x = 0.0$, 0.1, 0.2, 0.3, 0.4) are in the range of nanometer. All XRD peaks are correspondent with the JCPDS card no. 89-1092 (Zn Fe_2O_4) and 22-1086 ($CoFe_2O_4$) [23] and all peaks are related to the spinel structure. Average crystallite size for all samples was obtained as 29 nm, 25 nm, 24 nm, 22 nm and 21 nm for $x = 0.0$, $x = 0.1$, $x = 0.2$, $x = 0.3$, and $x = 0.4$ respectively. The lattice constant (a), measured as a function of Zn concentration in Table 1. It is observed that the lattice constant increases with the Zn concentration in the lattice. This is also reported by Gul et al. [24] and Vaidyanthan et al. [10] that lattice constant increases with Zn substitution. This is due to the fact that the radius of Co ions (0.78 Å) is smaller that that of Zn ions (0.82 Å). Therefore as the concentration of Zn ions increases the lattice constant also increases. The increase in lattice constant obeys the Vegard's Law. Fig. 2 shows variation of lattice constant with varied Zn concentration. It shows almost linear increase in lattice constant with zinc concentration. The uniform increase in lattice constant with Zn substitution indicates that lattice expands without disturbing the symmetry of lattice [16].

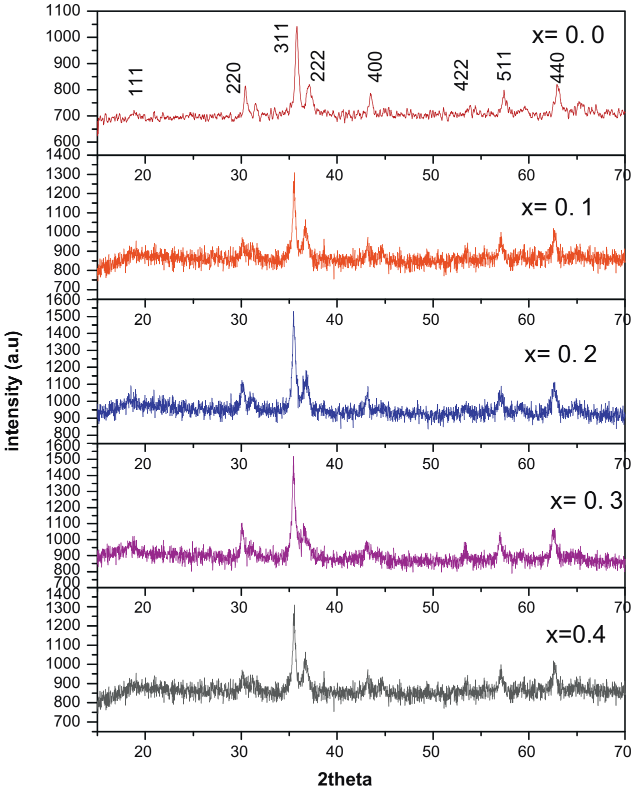

Fig. 1. The XRD patterns of $Co_{(1-x)}Zn_xFe_2O_4$ ($x = 0.0$, $x = 0.1$, $x = 0.2$, $x = 0.3$, $x = 0.4$) nanoferrite samples.

Fig. 3 shows TEM images of the $x = 0.1$ and $x = 0.4$ samples. TEM images of prepared CZFO nanoferrite are uniform and of spherical nature. The particle size obtained from the distribution is in the range of 20–30 nm.

3.2. Mössbauer analysis at room temperature

Fig. 4(a) shows the Mössbauer spectra of CZFO nanoferrites ($x = 0.0$, 0.1, 0.2, 0.3, 0.4) obtained at room temperature. Mössbauer spectroscopy is useful method for investigating the

Table 1

Crystallite size (*D*), lattice constant (*a*), hyperfine field (*H*) (Tesla), isomer shift (mm/s), magnetization (Ms) (emu/g), coercivity (Hc) (Oe), remanent magnetization (Mr) (emu/g) of $Co_{(1-x)}Zn_xFe_2O_4$ ($x = 0.0$, $x = 0.1$, $x = 0.2$, $x = 0.3$, $x = 0.4$) nanoferrite samples.

X (zinc concentration)	Crystallite size *D* (nm)	Lattice constant *a* (Å)	Hyperfine field (T)	Isomer shift (mm/s)	Magnetization (Ms) (emu/g)	Coercivity (Hc) (Oe)	Remanent magnetization (Mr) (emu/g) (300 K)
0.0	29	8.377	36.03	0.40	47.05	161.07	26.53
0.1	25	8.380	41.44	0.49	56.74	693.86	14.86
0.2	24	8.385	40.27	0.15	54.51	361.38	11.05
0.3	22	8.390	35.79	0.14	53.58	176.03	6.87
0.4	21	8.396	32.50	0.12	52.27	50.12	4.14

distribution of Fe ions over various sublattices. Results showed the simultaneous presence of a central paramagnetic doublet and a magnetically split component. The intensity of the central paramagnetic doublet increases with respect to magnetic sextet with increasing Zn concentration. The central doublet can be attributed to the magnetically isolated Fe^{3+} ions which do not participate in the long range magnetic ordering due to a large number of nonmagnetic nearest neighbors [25]. Mössbauer Spectra for $x = 0.2$, $x = 0.3$, $x = 0.4$ nanoferrites show the collective magnetic excitations. Which means a simultaneous presence of a central paramagnetic doublet and a magnetically split component. Fig. 4(b)–(d) shows the *p*–*B* distribution derived from the Mössbauer spectra of $x = 0.2$, $x = 0.3$, $x = 0.4$, nanoferrite respectively. It can be seen that the spectrum has a wide range of hyperfine magnetic field (HMF) distribution. The average hyperfine field for nano samples is given in Table 1. It is observed that magnetic hyperfine field decreases with increasing Zn concentration [Table 1]. The observed variations in hyperfine magnetic field can be qualitatively explained using Neel's super exchange interactions [26]. The replacement of Fe^{3+} by Zn^{2+} weakens the A–B super exchange interactions and hence hyperfine field is expected to decrease with increasing concentration of Zn. A similar decrease in hyperfine field with Zn concentration in place of Fe^{3+} has been reported by Waffaa Bayumi [25]. The values of isomer shift [Table 1] for the A and B sites consistent with high spin Fe^{3+} charge state [27].

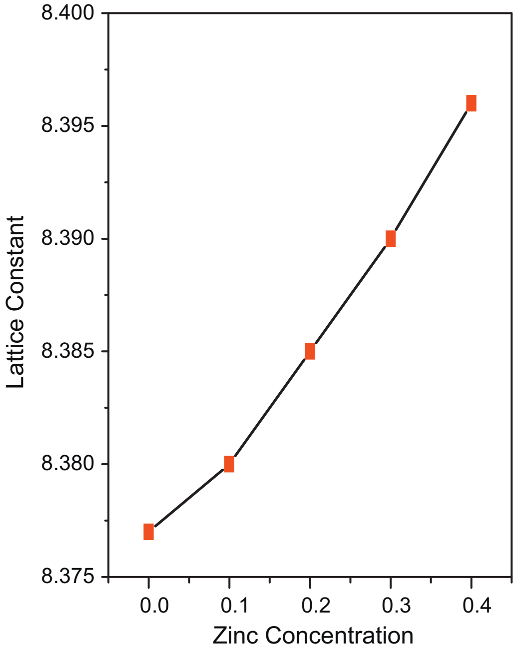

Fig. 2. Lattice constant of $Co_{(1-x)}Zn_xFe_2O_4$ ($x = 0.0$, $x = 0.1$, $x = 0.2$, $x = 0.3$, $x = 0.4$) with zinc concentration.

3.3. Magnetic studies at room temperature (300 K)

The magnetic properties of the powder samples have been determined at room temperature using SQUID with an applied field up to 60 kOe. Fig. 5 shows the variation of magnetization with the applied field for all five samples. Nano samples attain saturation magnetization in the applied field. All prepared samples of CZFO ($x = 0.0$, 0.1, 0.2, 0.3, 0.4) at room temperature exhibit ferrimagnetic coupling. Both saturation magnetization and coercivity decreases with Zn concentration at room temperature [Table 1]. The magnetic order in the cubic spinels is due to the super-exchange interaction mechanism occurring between the metal ions in the tetrahedral A-sites and octahedral B-site sublattices [28]. Substitutional ions (Zn^{2+}) with zero magnetic moment cause the variation in the magnetic properties of the spinel ferrites. The results obtained are in well accordance with the earlier reported values by Vaidyanathan et al. [29] and by Islam et al. [30]. The saturation magnetization increases from 47.05($x = 0.0$) to 56.74($x = 0.1$) emu/g. This is due to Zn^{2+} ion with zero magnetic moment replace ion on the tetrahedral A-site, which causes the decrease of magnetic

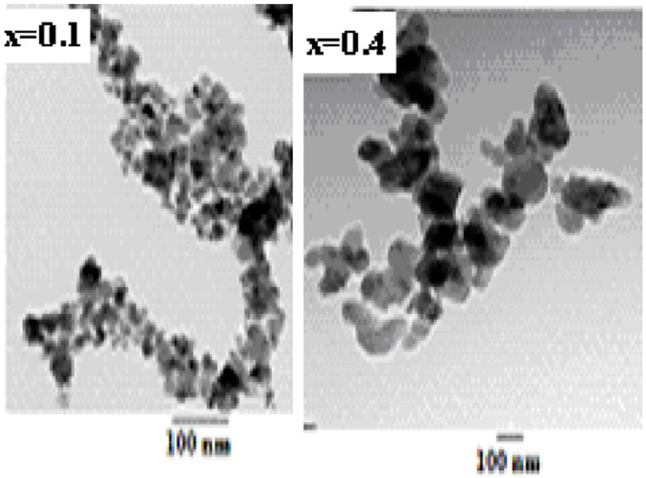

Fig. 3. TEM images of $Co_{(1-x)}Zn_xFe_2O_4$ nanoferrite samples ($x = 0.1$ and $x = 0.4$).

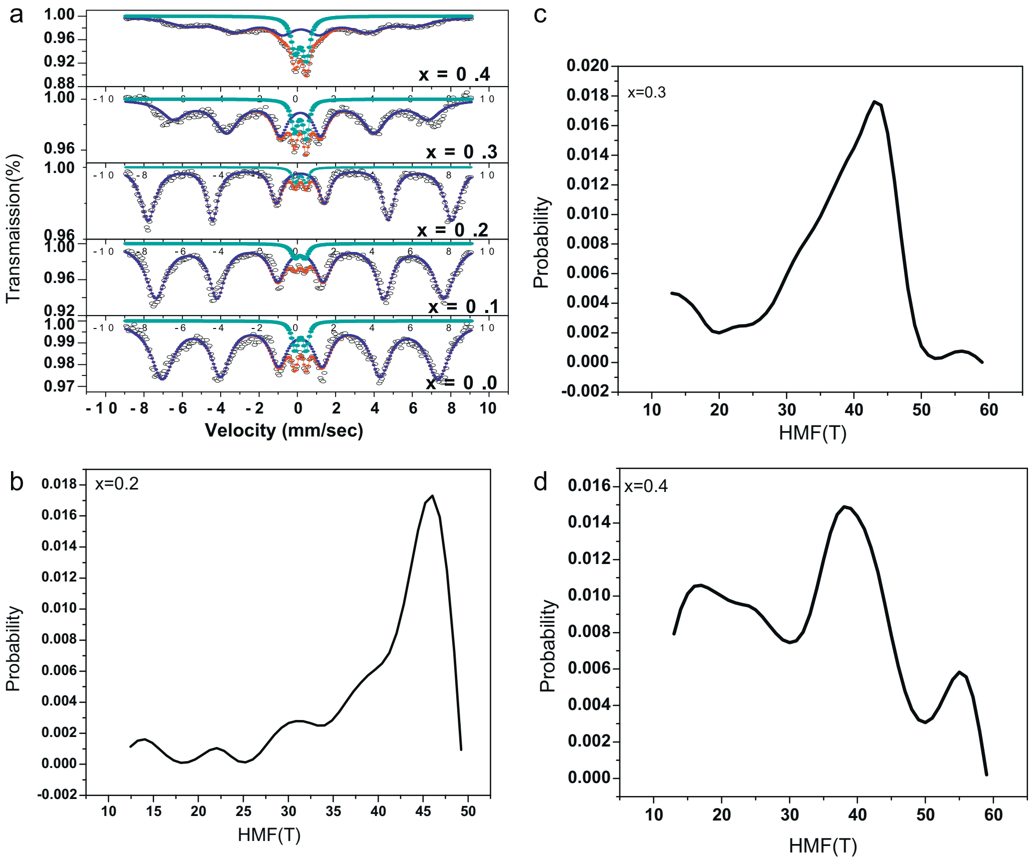

Fig. 4. (a) Mössbauer spectra of $Co_{(1-x)}Zn_xFe_2O_4$ ($x = 0.0$, $x = 0.1$, $x = 0.2$, $x = 0.3$, $x = 0.4$) nanoferrite samples at room temperature, and (b), (c), (d) *p–B* distribution of the samples ($x = 0.2$, $x = 0.3$, $x = 0.4$).

moment in the M_A sublattice, which results in an increase of total magnetic moment. When Zn concentration further increased from $x = 0.1$ to $x = 0.4$ the saturation magnetization decreases, due to the exchange interaction between A and B sites gets lowered resulting in strengthening of B–B interaction, which leads to decrease in magnetization. The coercivity also decreases with Zn concentration; this can be attributed to the non magnetic character of Zn ion. Since more Zn ions replace with Co ions by increasing '*x*' the saturation magnetization and coercivity decreases. The reverse is reported by Koseoglu et al. [13] he showed that saturation magnetization and coercivity increases with increasing Co content because Co is magnetic in character and of anisotropic nature. The variation of saturation magnetization, coercivity and remanence with Zn concentra-

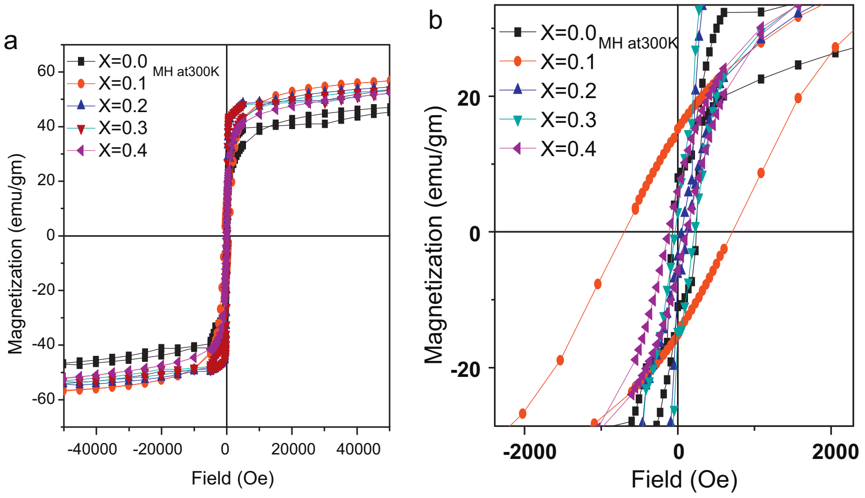

Fig. 5. (a) Variation of magnetization with applied field at 300 K for $Co_{(1-x)}Zn_xFe_2O_4$ ($x = 0.0$, $x = 0.1$, $x = 0.2$, $x = 0.3$, $x = 0.4$) nanoferrite samples. (b) Part of the curves near the origin showing remanence and coercivity.

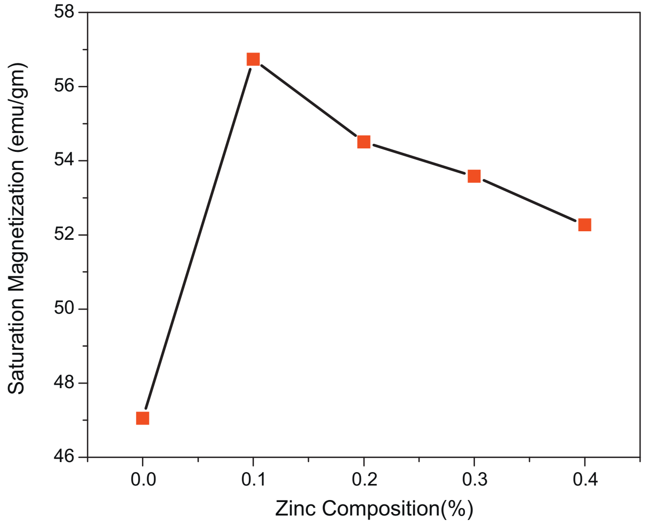

Fig. 6. Saturation magnetization of $Co_{(1-x)}Zn_xFe_2O_4$ ($x = 0.0$, $x = 0.1$, $x = 0.2$, $x = 0.3$, $x = 0.4$) nanoferrite samples with zinc composition.

tion is shown in Fig. 5(a) and (b) and Fig. 6. The results of M–H at room temperature are well supported by Mössbauer results at room temperature (Fig. 6).

4. Conclusion

CZFO nanoferrites with varied concentration of Zn are successfully prepared by solution combustion method. The lattice constant was found to increase with the increase in Zn concentration. The magnetic parameters such as saturation magnetization, remanent magnetization and coercivity were found to decrease with the increase in Zn substitution. Magnetic ordering of CZFO nanoferrite decreases with increase in Zn concentration. Saturation magnetization first increases and then decreases with increase in Zn concentration at room temperature. The Mössbauer spectra revealed that the hyperfine field decrease with increase in Zn concentration.

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