

Magnetic and magnetostrictive properties of $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles produced by co-precipitation method

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Abstract

$\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0-0.5$) nanocrystalline powders were prepared by co-precipitation method. The crystal structures and magnetic properties of the samples products were identified by x-ray diffractometer and vibrating sample magnetometer, respectively. XRD analysis reveals that $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanocrystalline powders occurred during a cubic spinel structure. The vibrating sample magnetometer investigations indicate that the saturation magnetization and the magnetic moment values increase with increasing Zn-content. The increase of saturation magnetization and magnetic moment is related to the strong magnetic property of Zn^{2+} . The coercive field of the samples varies linearly from 1137.77 Oe to 33.31 Oe. The decrease of coercive field is ascribed to the decrease in the content of Co^{2+} on the B sites. The results show that $x = 0.5$ in $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ is an optimum composition with superior magnetostrictive properties for many applications.

1. Introduction

Magnetostriction is the change in the dimensions of magnetic materials in the presence of the applied magnetic field. These changes occur when the material is cubic but the magnetic order is non cubic. If the material shrinks in the direction of applied magnetic field the magnetostriction is considered to be negative and if it expands, then it is termed as positive magnetostrictive [1]. Magnetostrictive smart materials are widely used as sensors as well as actuators in a variety of applications in the aerospace and automobile industries for vibration control and stress sensing, apart from other important applications in ultrasonic generation and detection, sonar, magnetostrictive filters, etc [2,3]. The Co-Zn ferrite [CZFO] has spinel structure with the metal ions distributed among 8 tetrahedral (A) and 16 octahedral coordinated (B) sites per unit cell in which oxygen atoms form a face-centered cubic (FCC) lattice. The unit cell requires eight (2^+) cations and sixteen (3^+) cations to maintain charge neutrality. However these do not correspond directly to A and B sites since occupancy is influenced by a combination of metal ion size, metal ion charge, ligand field stabilization energies and ultimately governed by the synthetic route [4-6]. Zhao et al. [7] studied the change in the magnetic properties of CoFe_2O_4 synthesized by emulsion method after substitution of Fe^{3+} by Nd^{3+} ions and the results revealed that the saturation magnetization is decreased and the coercivity is increased by increasing of Nd^{3+} ions addition. Yan et al. [8] used sol-gel route to show the effect the doping of cobalt ferrite thin films by Tb^{3+} ions and they found that the difficult crystallization and lattice distortion to a certain degree are obtained as a result for increasing the substitution by Tb^{3+} ions to 0.3 because of the large radius of Tb^{3+} ions [8]. Rashad et al. [9] have studied the magnetic properties of nanocrystalline Sm-substituted CoFe_2O_4 synthesized by citrate precursor method and they revealed that the saturation magnetization and coercive field are strongly dependent on the calcinations temperature and structure of the formed

powders. The saturation magnetization decreased by increasing the Sm content and increasing the calcination temperature from 400 to 800 °C. In the present work, $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5) ferrites have been prepared by co-precipitation method. For the single phase of the prepared samples, the bond lengths between the cation-cation (M_e-M_e) and between the cation-anion (M_e-O) were calculated using the experimental values of the lattice constant. The oxygen positional parameter was determined using x-ray diffraction data. Measurements of saturation magnetization, magnetic moment and coercivity have been carried out to characterize the magnetic properties.

2. Experimental

The $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ sample was synthesized using Cobalt acetate $[(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}]$, Zn acetate $[(\text{CH}_3\text{COO})_2\text{Zn} \cdot 4\text{H}_2\text{O}]$ and Fe nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ as precursors, by dissolving them in distilled water in the required mole proportion. The clear solution was co-precipitated with a 1 molar NaOH solution at fixed temperature of 100 °C. Samples at this stage are referred 'as prepared'. The precipitate was filtered and then washed several times with distilled water until the pH of the filtered water became 7 (i.e., neutral). The filtrate was then dried at 100 °C overnight. The dried powders were then used to make pellet with a die of diameter 10 mm. The hand press machine was used to apply pressure of about 5–6 ton for 5 minutes to make the pellets. The diameter of the 2 to 3 mm thick pellet was 10 mm. All the samples further sintered at 700 °C for the same time interval of 6 h to compare the electrical and dielectric properties of the samples. The samples of $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ where $x = 0.0, 0.1, 0.2, 0.3, 0.4$, and 0.5 sintered at 700 °C are referred as C_1, C_2, C_3, C_4, C_5 , and C_6 respectively. The single-phase formation of the materials was confirmed by powder X-ray diffraction (XRD) technique. X-ray diffractogram of all the samples was recorded using an X-ray diffractometer (model Bruker D8 Advance).

The hysteresis properties such as saturation magnetization (M_s), magnetic moment (η_B) and coercive force (H_c) were obtained from high field hysteresis loop tracer working at 50 Hz mains frequency.

3. Results and discussion

3.1 Structural analysis

The XRD patterns of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ where $x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5 are shown in Fig. 1. All the patterns were indexed using JCPDS data for Co-Zn ferrite and reveal a cubic spinel structure.

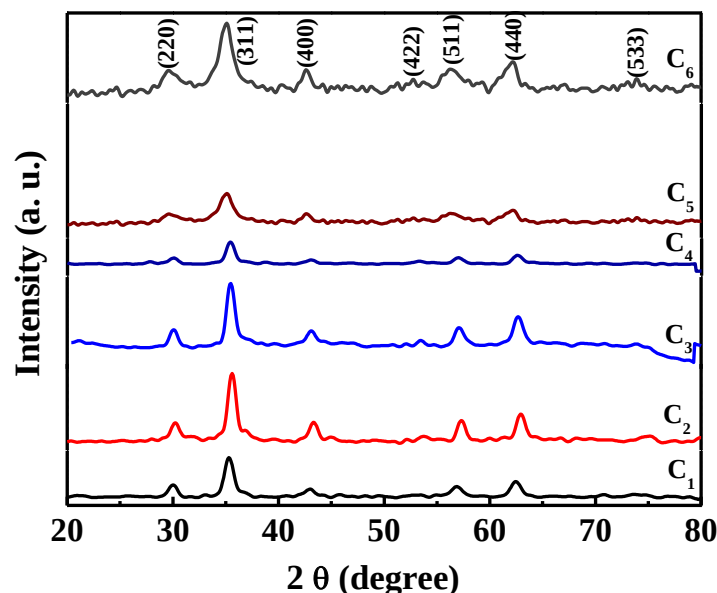


Fig. 1 XRD patterns of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0-0.5$).

The lattice constant "a" obeys Vegard's law, indicating thereby its increasing trend with Zn-content. The lattice constant increases from 8.38 Å to 8.41 Å with increasing x . This suggests the strong occupancy of Zn^{2+} ion on tetrahedral (A) site and Co^{3+} ion on the octahedral (B) site. Similar explanation can be concluded in case of Zn-Mg ferrite substituted by Nd^{+3} [10]. The crystallite size of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ was determined using the well-known Scherrer's equation [11].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad \dots\dots\dots(1)$$

Where D is the crystallite size, λ is the X-ray wavelength, θ is the Bragg's angle and β is the full width of the diffraction line at half the maximum intensity. The crystallite size observed is in the range of 21.32 nm to 53.41 nm.

In ferrites, the metallic ions occupy two crystallographically different sites, A sites (tetrahedral) and B sites (octahedral). Three kinds of magnetic interactions are possible between the metallic ions through the intermediates O^{2-} ions, by super exchange mechanism namely, A-A interactions, B-B interactions and A-B interactions. It is observed that the interaction energies between two magnetic ions M^I and M^{II} depend on the distance of these ions from the oxygen ions through which interactions occur and the angle between $M^I - O - M^{II}$ represent by θ . The angle θ of about 180° between the cations given maximum interaction energy. The exchange energy decreases rapidly with increasing distance of the cations from the oxygen anion. The various possible configurations of the ion pairs in spinel ferrites with favourable distances and angles for an effective magnetic interaction as by Gorter [12] are given in Fig 2.

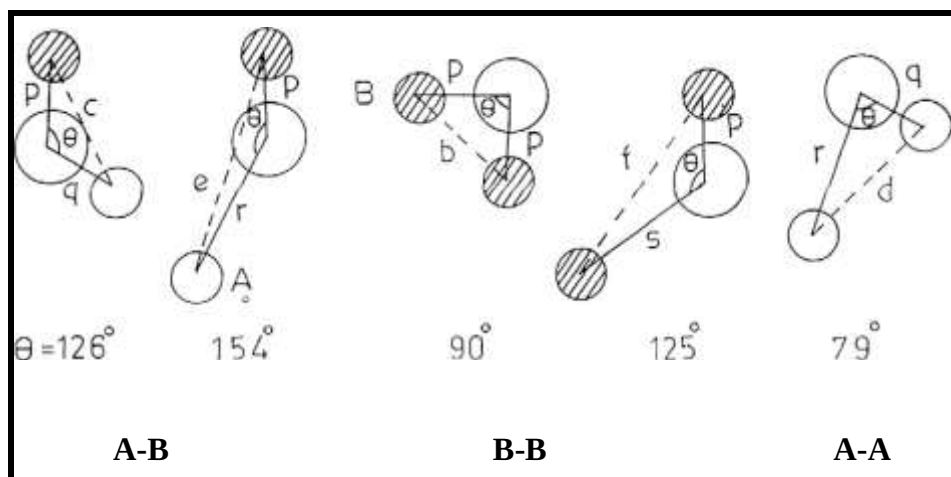


Fig. 2. Configurations of the ion pairs in spinel ferrites with favorable distances and angles for effective magnetic interactions.

The bond lengths between the cations (b , c , d , e and f) ($Me-Me$) and between the cations and anions (p , q , r and s) ($Me-O$) were calculated using the experimental values of lattice constant and the oxygen positional parameter (u) by the following relations [13-15]:

$$\begin{aligned} \text{Me-O} & & \text{Me-Me} \\ p = a(1/2 - u) & & b = (a/4)2^{1/2} \\ q = a(u - 1/8)3^{1/2} & & c = (a/8)11^{1/2} \end{aligned}$$

$$\begin{aligned} r &= a(u - 1/8)11^{1/2} & d &= (a/4)3^{1/2} \\ s &= a/3(u + 1/2)3^{1/2} & e &= (3a/8)3^{1/2} \\ f &= (a/4)6^{1/2} \end{aligned}$$

It is seen that the bond lengths $Me-O$ and $Me-Me$ increase with increasing x . The increase in $Me-O$ and $Me-Me$ distances should result in the weakening of the strength of interatomic bonding and as a result one can expect a reduction in the Néel temperature on Zn substitution.

Table 1. Interionic distances between cation-anion ($Me-O$) and cation-cation ($Me-Me$).

Samples	$Me-O$ (Å)				$Me-Me$ (Å)				
	p	q	r	s	b	c	d	e	f
C1	2.0112	1.959	3.752	2.122	2.962	0.107	0.113	5.443	5.132
C2	2.0044	1.976	3.783	2.120	2.965	0.108	0.113	5.448	5.136
C3	1.998	1.989	3.810	2.119	2.967	0.108	0.113	5.451	5.139
C4	1.991	2.005	3.840	2.118	2.969	0.108	0.114	5.454	5.143
C5	1.985	2.020	3.869	2.117	2.971	0.109	0.115	5.459	5.146
C6	1.978	2.036	3.899	2.116	2.973	0.109	0.116	5.462	5.150

The cation distribution in $Ni_{1-x}Zn_xFe_2O_4$ can be inferred from the x-ray diffraction relative integrated intensity calculations by using the following formula suggested by Buerger [16].

$$I_{hkl} = |F|_{hkl}^2 PL_p \dots \dots (2)$$

Where I_{hkl} is the relative integrated intensity, F is the structure factor, P is the multiplicity factor and L_p is the Lorentz-polarization factor which depends only on the Bragg's diffraction angle (θ).

$$L_p = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos 2\theta} \dots \dots (3).$$

According to Ohnishi and Teranishi [17], the intensity ratios of planes $I(200) / I(400)$, $I(220) / I(422)$ and $I(400) / I(422)$ are considered to be sensitive to the cation distribution parameter (x). The

ionic configuration based on site preference energy values proposed by Miller [18] for individual cations in $Co_{(1-x)}Zn_xFe_2O_4$ suggest that Co^{2+} and Fe^{3+} have strong B-site, while Zn^{2+} and Fe^{3+} ions occupy the A-sites. There is a good contrast in the atomic scattering factors of Fe^{3+} and the other cations present in the system. This makes the determination of cation distribution quite reliable. Moreover, any alternation in the distribution of cations causes a significant change in the theoretical values of x-ray diffraction intensity ratios. Therefore, in the process of arriving at the final cation distribution, the site occupancy of all the cations was varied for many combinations and those that agree with the experimental intensity ratios, which are shown in Table 2.

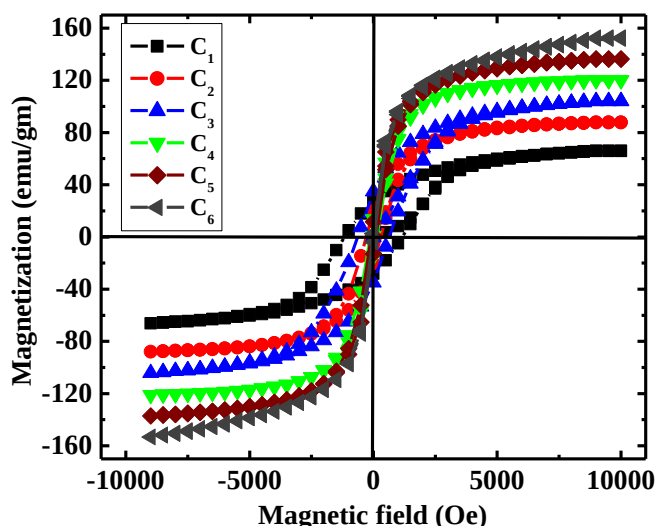
Table 2 Comparison of x-ray intensity ratios for estimating cation distribution.

Samples	A- sites	B-sites	$I(220)/I(400)$	$I(220)/I(440)$	$I(400)/I(422)$
C ₁	Fe ³⁺	Co ²⁺ .Fe ³⁺	1.23 1.25	0.48 0.44	0.50 0.52
C ₂	Zn ²⁺ _{0.1} Fe ³⁺ _{0.9}	Co ²⁺ _{0.9} .Fe ³⁺ _{1.1}	1.24 1.21	0.42 0.47	0.43 0.48
C ₃	Zn ²⁺ _{0.2} Fe ³⁺ _{0.8}	Co ²⁺ _{0.8} .Fe ³⁺ _{1.2}	1.26 1.22	0.45 0.48	0.46 0.43
C ₄	Zn ²⁺ _{0.3} Fe ³⁺ _{0.7}	Co ²⁺ _{0.7} .Fe ³⁺ _{1.3}	1.20 1.18	0.47 0.46	0.40 0.42
C ₅	Zn ²⁺ _{0.4} Fe ³⁺ _{0.6}	Co ²⁺ _{0.6} .Fe ³⁺ _{1.4}	1.19 1.21	0.43 0.39	0.47 0.41
C ₆	Zn ²⁺ _{0.5} Fe ³⁺ _{0.5}	Co ²⁺ _{0.5} .Fe ³⁺ _{1.5}	1.17 1.14	0.40 0.41	0.38 0.41

3.2 Magnetic and magnetostrictive properties

Typical magnetic hysteresis loops for Co_(1-x)Zn_xFe₂O₄ ferrites where x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5 are shown in Fig. 3. It is clear that the saturation magnetization (M_s) increases with increasing Zn-concentration. The increase in saturation magnetization may be primarily due to the substitution of nonmagnetic Zn ion (d¹⁰) for Co into the magnetic ferrite lattice. Zn²⁺ has a stronger preference for the tetrahedral site (A site), while Co²⁺ ions (for which Zn is substituted) are located on octahedral site (B site) of AB₂O₄ spinel ferrite. Thus, Zn displaces Fe³⁺ from A to B site. As the magnetic spin of neighboring A and B sites are anti-ferromagnetically coupled (due to the super exchange interaction in ferrite lattice), the net result is an increase in magnetic moment on B sub-lattice, as well as the increase of the net magnetic moment of the

crystal [17], while the value of H_c decreases with increasing Zn-content, which may be due to that the particle size is less than the critical size of single domain. In this range of particle size, the H_c variation dependence on the particle size can be explained by Stoner-Wohlfarth theory [19]. According to the theory, the coercivity (H_c) of a single domain particle is $H_c = 2K/\mu_0 M_s$, where K is the magnetocrystalline anisotropy constant, μ_0 is the universal constant of permeability in free space and M_s is the saturation magnetization of the particles. The increase of Zn content results in complete crystallization, hence the value of K decreases, while M_s increases with increasing the particle size, so the variation of K and M_s seems to contribute to the corresponding H_c decrease in accordance with Fig. 3. The values of M_s, η_B and H_c of the Co_(1-x)Zn_xFe₂O₄ ferrites are listed in Table 3.

Fig.3 Hysteresis of Co_(1-x)Zn_xFe₂O₄ composites where x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5.Table 3 Saturation magnetization (M_s), magnetic moment (η_B) and coercive field (H_c) of the Co_(1-x)Zn_xFe₂O₄ ferrites

Mole % of Zn-content (x)	M _s (emu/gm)	η_B (μ_B)	H _c (Oe)
C ₁	71.297	3	1137.77
C ₂	87.710	3.7	635.5
C ₃	104.038	4.4	271.111
C ₄	120.285	5.1	128.88
C ₅	136.449	5.8	88.80
C ₆	152.531	6.5	33.31

3.3 Magnetostrictive properties of ferrites

Figure 4(a-b) shows the variation of transverse magnetostriction (λ_{11}) and longitudinal (λ_{12}) with dc magnetic field for $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$. It is seen from the figure that, λ_{11} is negative while λ_{12} is positive in the magnetic field range of measurements. The magnetic field dependent magnetostriction (λ_{ij}) values i.e. both λ_{11} and λ_{12} increases with different rates. The magnetostriction values increase rapidly in the low magnetic field region up to 5 kOe. Both λ_{11} and λ_{12} shows saturation at higher fields above 4 kOe for the samples $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ with $x=0, 0.1, 0.2, 0.3, 0.4$, and 0.5 whereas λ_{11} and λ_{12} keep on increasing with decreased rate in the high field region. The maximum value of λ_{11} and λ_{12} for

CoFe_2O_4 are 139 and 59 respectively. The maximum values observed in the present case are higher than that of literature values [20,21]. This may be due to the method of preparation, sintering temperature and grain size effect for the present sample. It is interesting to note that the continuous doping of Zn in CoFe_2O_4 decreases the values of overall magnetostriction as expected. It is seen from Fig. 4 that as Zn content in place of Co goes on increasing the maximum value of magnetostriction (λ_{max}) goes on decreasing from 59 to 5 and the value of magnetic field at which λ reaches its maximum value increases from 3597 Oe to 10000 Oe respectively. This behavior is due to enhanced anisotropy with substitution of Zn in CoFe_2O_4 .

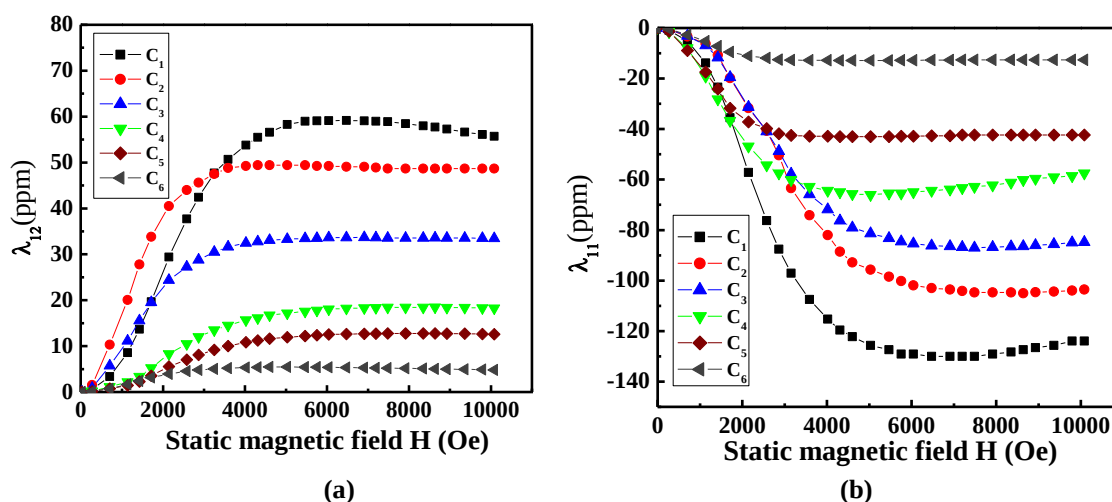


Figure 4 (a-b) Variation of magnetostriction coefficient λ_{11} and λ_{12} with dc magnetic field for $\text{Ni}_x\text{Co}_{(1-x)}\text{Fe}_2\text{O}_4$.

Figure 5(a-b) shows the variation of piezomagnetic coefficient (q) with dc magnetic field for $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples. The piezomagnetic coefficient can be calculated as $q_{ij} = (d\lambda_{ij}/dH)$. Hence the value of q was calculated for both the transverse and longitudinal mode and is represented as q_{12} and q_{11} respectively. The magnetic field dependent piezomagnetic coefficient shows peak behavior. This behavior can be understood on the basis of magnetic field dependent magnetostriction coefficient variation. As the magnetostriction coefficient increases with increasing magnetic field, the slope q

($d\lambda/dH$) also increases. Furthermore, as the magnetic field increases, λ starts to saturate which in turn decreases the slope q . Another interesting phenomenon is that, for both q_{11} and q_{12} , the peak positions obtained for the same sample are different. This is due to the difference in the magnetic field dependent behavior for both λ_{11} and λ_{12} . Hence in Co rich ferrites the piezomagnetic peak positions are observed in the high magnetic field region, whereas the Zn rich samples show piezomagnetic peak positions in higher magnetic field region [22].

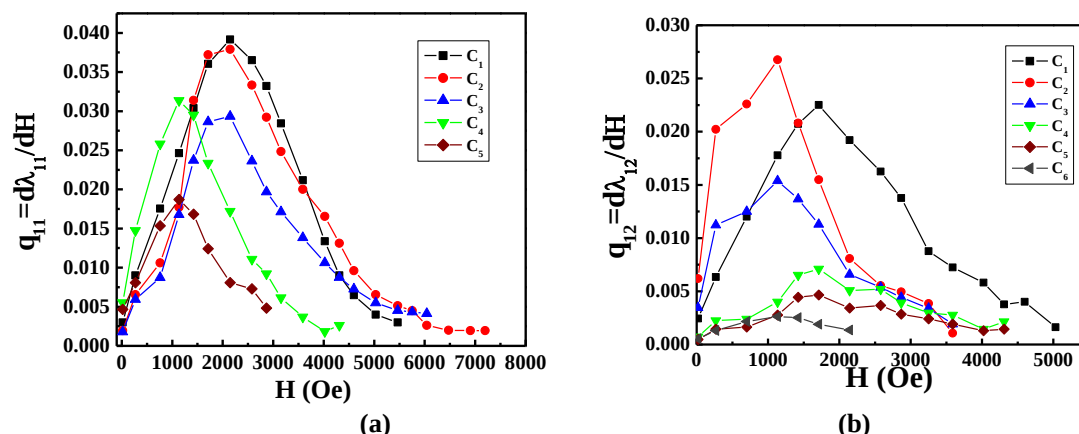


Figure 5 (a-b) Variation of piezomagnetic coefficient q_{11} and q_{12} with dc magnetic field for $\text{Ni}_x\text{Co}_{(1-x)}\text{Fe}_2\text{O}_4$.

4. Conclusions

Using Co-precipitation method, $\text{CoZnFe}_2\text{O}_4$ nanoparticles have been synthesized. The effect of Zn ratios content from $x = 0$ to $x = 0.5$ on the crystal structural and magnetic properties of the produced cobalt ferrite have been studied in details. The results showed that the lattice constant increases with increasing Zn content. The variation in lattice

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constant can be ascribed to the difference in the ionic size of the component. The magnetic properties are studied using M-H loops. It is observed that the room temperature magnetic parameters have strong dependency on the Zn content. The variation of magnetostriction and piezomagnetic coefficients with applied magnetic field behavior depend on the doping content of Zn in CoFe_2O_4 .

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الخواص المغناطيسية والتشكيلية المغناطيسية للجسيمات النانوية لمركبات $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ المحضرة باستخدام طريقة الترسيب

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الملخص

تم تحضير مساحيق بلورية دقيقة لمركبات $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ باستخدام طريقة الترسيب. ان التركيب البلوري والخواص المغناطيسية لهذه المساحيق قد شخصت بواسطة حيود الاشعة السينية وجهاز الاهتزاز المغناطيسي على التوالي. ان التشخيص بالاشعة قد اظهر بان المساحيق الدقيقة اعلاه ذات تركيب بلوري مكعبي الشكل بينما اظهرت الفحوصات المغناطيسية ان الاشباع المغناطيسي والعزم المغناطيسي يزدادان بزيادة تركيز Zn^{+2} . ان شدة التلاصق للنماذج تتغير بشكل خطي من 1137.77 Oe الى 33.31 Oe . ان قلة شدة التلاصق لهذه النماذج تعزى الى قلة محتوى ال Co^{+2} في موقع B. اظهرت النتائج ان قيمة x عندما تكون 0.5 في المركب $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ هي قيمة مثالية لهذه الجسيمات حيث تكون لها خواص مغناطيسية مع العديد من التطبيقات.