

Synthesis and Characterizations of Zirconium (Zr⁴⁺) Substituted Cobalt Ferrite (CoFe₂O₄) Nanoparticles Synthesized Via Sol-Gel Auto Combustion Technique

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Abstract: *The present work focuses on the effect of zirconium (Zr⁴⁺) substitution on structural, microstructural and infrared studies of the nanocrystalline cobalt ferrite (CoFe₂O₄). The samples of Co_{1-x}Zr_xFe_{2-2x}O₄ nanocrystalline spinel ferrite of different compositions with x = 0.0, 0.1, 0.2 and 0.3 have been synthesized by sol-gel auto combustion method. Citric acid (C₆H₈O₇) was used as a fuel; the pH was maintained at 7 and the prepared samples were sintered at 600 °C for 4 h. The structural properties were estimated from X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) studies. The microstructural studies were investigated through Scanning electron microscopy (SEM) technique. The average particle size was calculated by using Debye Scherer's formula using XRD data and is obtained to be 14-26 nm. The average grain size was found to be in nanometer range and of the order of 16-28 nm obtained by using SEM images. The IR spectra show two principle absorption bands in the range of 400 cm⁻¹ to 1000 cm⁻¹.*

Keywords: *nanocrystalline, cobalt ferrite, sol-gel, XRD, SEM, FTIR.*

1. INTRODUCTION

Ferrites are the ferrimagnetic materials which possess the combined properties of magnetic conductor and electrical insulator. They have been extensively investigated and being a subject of great interest because of their importance in many technological applications such as antenna rods, transformer cores, magnetic data storage [1]. These electrical and magnetic properties are affected by the type of the substituent, microstructure, chemical composition and method of preparation [2, 3]. The ferrites are commonly prepared by ceramic technique which involves high temperature sintering and prolong heating. This method produces particles of coarse nature. The ceramic method has some inherent drawbacks and do not produce particles of small sizes of the order of nanometer. In the recent years, nanosize spinel ferrite particles received a considerable attention because of their interesting magnetic properties [4]. It is found that when the particle diameter reduce to nanometer dimension spinel ferrite particles may exhibit super paramagnetic behaviour, which is of great interest from the point of view of their applications [5]. Spinel ferrites are compounds of iron oxides and some transition metal oxides and they exhibits important electrical and magnetic properties, which made them extensively useful in technological and industrial applications such as magnetic storage in microwave devices [6, 7]. Cobalt ferrite is a well known hard magnetic material with inverse spinel structure. The saturation magnetization and coercivity of cobalt ferrite is higher than the other nickel, manganese spinel ferrites [8]. Cobalt ferrite is the most important and abundant magnetic materials that have large

magnetic anisotropy, moderate saturation magnetization, remarkable chemical stability and mechanical hardness, which make it good candidate for the recording media [9, 10].

The chemical composition method of synthesis, nature of dopant, site preference of dopants etc parameters strongly influences the structural, electrical and magnetic properties of spinel ferrites [11, 12]. Various substituents of magnetic and nonmagnetic nature like Ni, Zn, Al, etc have been incorporated in cobalt ferrite to modify their properties. However, to our knowledge zirconium has not been substituted in cobalt ferrite. Zirconium is a lustrous, grayish-white, soft, ductile and malleable metal which is solid at room temperature, though it becomes hard and brittle at lower purities. Zirconium is highly resistant to corrosion by alkalis, acids, salt water and other agents.

In the present study, the effect of zirconium substitution in cobalt ferrite $\text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$, on structural, microstructural and infrared properties of nanocrystalline cobalt ferrite synthesized by sol-gel auto combustion are reported. Zirconium-containing compounds are used in many biomedical applications [13].

2. EXPERIMENTAL

2.1. Preparation of $\text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$ Spinel Ferrite Nanoparticles

Materials

The raw materials used for sol-gel auto combustion synthesis of $\text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0.0, 0.1, 0.2$ and 0.3) nanoparticles were cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), zirconium nitrate ($\text{ZrO}(\text{NO}_3)_2$), ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$). All the reagents used for the synthesis of cobalt ferrite nanoparticles were analytical grade and used as received without further purification.

Synthesis

$\text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0.0, 0.1, 0.2$ and 0.3) nanoparticles were synthesized by sol-gel auto combustion method using citric acid as a fuel. The stoichiometric proportions of metal nitrates to fuel (citric acid) ratio as 1:3 were taken into separate glass beakers. These were stirred for 15-20 minutes to dissolve completely into distilled water. After complete dissolution they were mixed together. Ammonia was added drop-wise into the solution to adjust pH value to about 7 and stabilize the nitrate-citric acid solution. Then the neutralized solution was constantly magnetically stirred and heated at 80-90 °C for 6 h on a hot plate. On the formation of sol-gel, very viscous gel the temperature was further raised up to 120 °C so that the ignition of the dried gel started and finally powder was obtained. The as prepared loose cobalt ferrite powder was grinded for 30 minutes and annealed at 600 °C for 6 h in muffle furnace.

2.2. Characterizations

In the present work, zirconium substituted cobalt ferrite samples were synthesized by sol-gel auto combustion method and characterized by X-ray diffraction technique. X-ray diffraction patterns of all the samples were recorded at room temperature by using a Regaku Miniflex-II X-ray powder diffractometer operated at 40 kV and 30 mA. The diffraction patterns were recorded in the 2θ range 20° to 80° with scanning rate of 2° per minute using Cu-K_α radiation of wavelength 1.5406 Å. Morphology of the prepared samples was studied using Scanning electron microscope (SEM) JEOL-JSM 840 Model. The infrared spectra of all the samples of the present series were recorded at room temperature in the range 400 cm^{-1} - 1000 cm^{-1} on FTIR-6100 type-A model. To study the IR spectra of all the samples, about one gram of fine powder of each sample was mixed with KBr in the ratio 1:250 by weight to ensure uniform distribution in the KBr pellet. The mixed powder was then pressed in a cylindrical die to obtain disc of approximately 1 mm thickness.

3. RESULTS AND DISCUSSIONS

The X-ray diffraction technique was used to characterize the prepared samples of $\text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0.0, 0.1, 0.2$ and 0.3) system. All the XRD pattern shows well defined reflections belonging to cubic spinel structure. Typical XRD pattern of the sample $x = 0.3$ is shown in Fig.1.

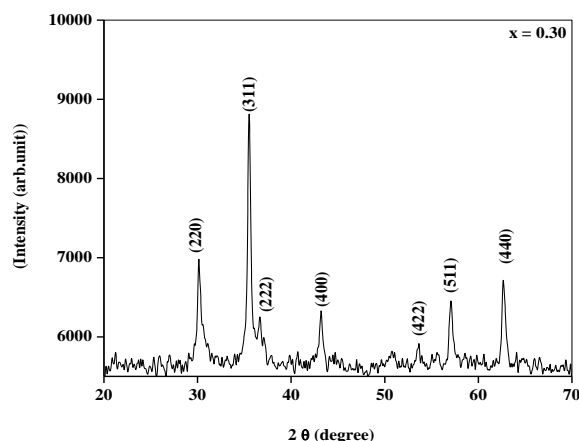


Fig 1. XRD pattern of $Co_{1+x}Zr_xFe_{2-2x}O_4$ ($x = 0.30$)

All the peaks in the XRD pattern were indexed by using Bragg's law. The presence of planes (220), (311), (222), (400), (422), (511) and (440) in the XRD pattern reveals the cubic spinel structure of all the samples. It is also evident that all the peaks are intense and sharp. No impurity peaks were observed, thus the samples are single phase in nature. It is also evident from XRD pattern that the intensity of Bragg's peak gets decreased on zirconium substitution. The peaks get broader with the substitution of Zr^{4+} ions. Similar XRD patterns have been observed for Mg doped Zn ferrites [14]. Table 1 gives the planes (h k l), corresponding Bragg's angles along with their interplanar spacing (d) values, intensity and intensity ratio of the $Co_{1+x}Zr_xFe_{2-2x}O_4$ ferrite system for typical sample $x = 0.3$.

Table 1. Miller indices (h k l), Bragg's angle (2θ), Interplanar spacing (d), Intensity (I) and Relative intensity ratio(I/I₀) of $Co_{1+x}Zr_xFe_{2-2x}O_4$ ($x = 0.30$)

(h k l)	2θ (degree)	d (Å)	I (a. u)	I/I ₀
(220)	30.10	2.9665	992	47
(311)	35.48	2.5280	2139	100
(222)	36.64	2.4506	391	19
(400)	43.16	2.0943	415	20
(422)	53.64	1.6878	214	11
(511)	57.04	1.6133	574	27
(440)	62.64	1.4848	990	47
(533)	73.78	1.2822	229	11

It is seen from the XRD data and XRD patterns that the interplanar spacing (d) values show gradual increase with increasing Bragg's angle for all the samples. The intensity of (311) plane is more as compared to other planes like (220), (222), (400), (422), (511) and (440). The Lattice constant (a) values of the zirconium substituted cobalt ferrite nanoparticles were calculated using standard relation,

$$a = d\sqrt{(h^2+k^2+l^2)} \quad \text{Å} \quad (1)$$

Where, (d) is interplanar spacing; (h k l) is Miller Indices.

The obtained values of the lattice constant (a) are tabulated in Table 2. The increase in lattice constant with zirconium content x can be interpreted on the basis of the ionic radii of the constituent ions Co^{2+} , Zr^{4+} , Fe^{3+} . The substitution of Zr^{4+} with Co^{2+} ions in place of two Fe^{3+} ions

leads to increase in lattice constant. Similar behaviour of lattice constant was reported in the literature [15].

Table 2. Lattice constant (a) and particle size (t) of zirconium substituted cobalt ferrite samples.

Composition 'x'	a (Å)	t (nm)
0.00	8.384	14
0.10	8.393	16
0.20	8.40	26
0.30	8.411	17

The particle size of the zirconium substituted cobalt ferrite powders was calculated by using the most intense peak (311) and using the Debye-Scherrer relation for small and uniform sized cubic crystals mentioned below [16] and is tabulated in Table 2.

$$t = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{nm} \quad (2)$$

Where, λ is wavelength of the Cu-K α radiation,

β is the full width of the half maximum

θ is Bragg's angle.

Morphology of the prepared samples was studied using Scanning electron microscope (SEM) where the secondary electron images were taken at different magnification to study the morphology. Fig. 2 represents the Scanning electron micrographs for typical $x = 0.30$ sample. Scanning electron micrographs indicates the formation of nano-sized grains of the $\text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$ ferrite powder.

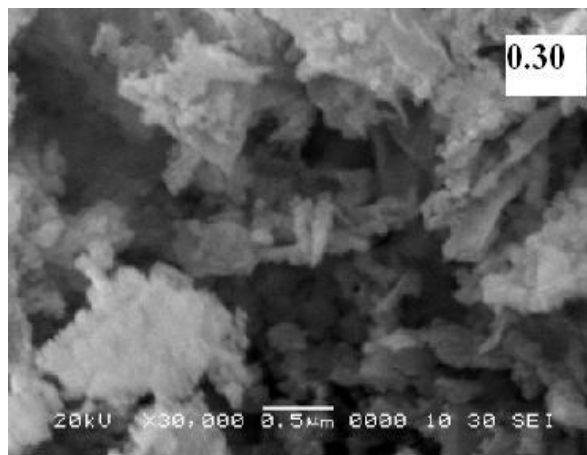


Fig 2. SEM image of $\text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0.30$)

The grain size was determined by linear intercept method estimated using the relation:

$$D = 1.5 L / M \cdot N \quad (3)$$

Where, L is a total test line length,

M is magnification

N is total number of the samples

The average grain size is found to be in nanometer range and of the order of 16-28 nm. From the SEM micrographs it is seen that the ferrite powder is an aggregation of particles. The particles observed as uniform grains confirm the crystalline nature of the ferrites. The specific surface area of all the samples using SEM images was calculated according to the relation:

$$S = \frac{6000}{D\rho} \quad (4)$$

Synthesis and Characterizations of Zirconium (Zr⁴⁺) Substituted Cobalt Ferrite (CoFe₂O₄) Nanoparticles Synthesized Via Sol-Gel Auto Combustion Technique

Where, D is particle diameter in nm,

ρ is density of the particles in gm/cm³.

The values of specific surface area are given in Table 3. The large value of specific surface area indicates the nanocrystalline nature of all the samples under investigation. The decrease in grain size increases the surface area.

Table 3. Particle size (t), Grain size (G) and Specific surface area (S) of Co_{1+x}Zr_xFe_{2-2x}O₄ system

Composition 'x'	t (nm)	G (nm)	S (m ² /g)
0.00	14	16	100.89
0.10	16	19	81.62
0.20	26	28	54.71
0.30	17	20	72.26

Infrared (IR) spectra of the Co_{1+x}Zr_xFe_{2-2x}O₄ (x = 0.0, 0.1, 0.2 and 0.3) nanocrystalline were recorded at room temperature. Fig.3 represents typical IR spectrum of the x = 0.3 sample. The IR spectrum shows the two principle absorption bands in the range of 400 cm⁻¹ to 1000 cm⁻¹, the first absorption band (ν_1) is seen at around 396.09 cm⁻¹ and second absorption band (ν_2) is around 578.94 cm⁻¹. The absorption bands (ν_1 and ν_2) correspond to intrinsic lattice vibrations of octahedral and tetrahedral coordination compounds in the spinel structure respectively.

The difference in frequency between the characteristic vibrations ν_1 and ν_2 may be attributed to the long bond length of oxygen-metal ions in the tetrahedral sites. The behaviour of ν_1 and ν_2 vibrations mainly depends on the identification of transition metal ions in the tetrahedral site and to a smaller extent on the ions situated at the octahedral sites. Similar type of IR spectra was observed for the Nd, Gd and Sm doped Co ferrite [17].

Table 4. Infrared absorption band (ν_1 and ν_2), Force constant (K_t and K_0), Bond length (R_A , R_B) of Co_{1+x}Zr_xFe_{2-2x}O₄ system

Composition 'x'	ν_1 cm ⁻¹	ν_2 cm ⁻¹	$K_t \times 10^5$ dyne/cm	$K_0 \times 10^5$ dyne/cm	R_A (Å)	R_B (Å)
0.00	703	479	2.10	1.400	0.644	0.682
0.10	708	429	2.15	1.192	0.652	0.697
0.20	712	421	2.18	1.181	0.660	0.704
0.30	720	416	2.24	1.186	0.668	0.710

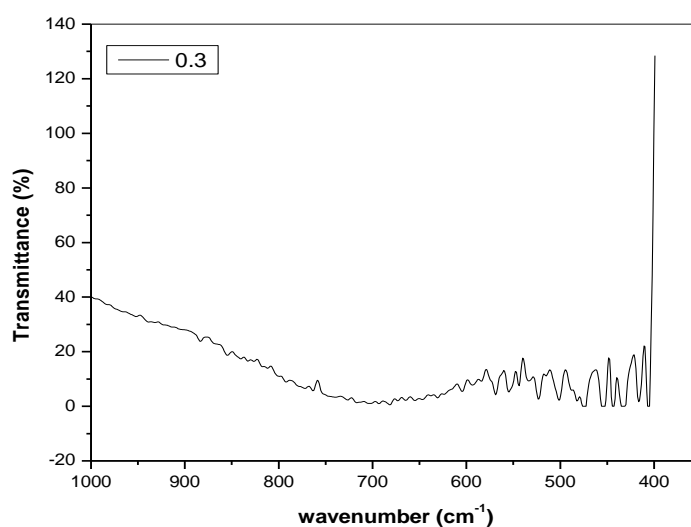


Fig 3. IR pattern of Co_{1+x}Zr_xFe_{2-2x}O₄ (x = 0.30)

According to Waldron, ferrites can be considered as continuously bonded crystals that also bonded to all nearest neighbours by equivalent forces (ionic, covalent or Vanderwal's). IR absorption bands of solids are usually assigned to the vibration of ions in the crystal lattice.

The force constant can be calculated for tetrahedral site (K_t) and octahedral site (K_o) by using the method suggested by Waldron [18]:

$$K_t = 7.62 \times M_A \times v_t^2 \times 10^{-7} \text{ N/m} \quad (5)$$

$$K_o = 10.62 \times (M_B/2) \times v_o^2 \times 10^{-7} \text{ N/m} \quad (6)$$

Where, M_A and M_B are the molecular weights of cations at A and B-sites, respectively.

The values of v_1 and v_2 and K_t and K_o are given in Table 3. It is observed from table that K_t and K_o both vary as per the variation in v_1 and v_2 values. No systematic variation in force constant was observed. The bond length corresponding to tetrahedral (A) and octahedral [B] sites was calculated and their values are listed in Table 3. It is seen from table 3 that both R_A and R_B increase with zirconium content x . The results on IR studies of the present samples are analogous to that reported in the literature [19]

4. CONCLUSIONS

The nanocrystalline $\text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$ spinel ferrite of different compositions with $x = 0.0, 0.1, 0.2$ and 0.3 were successfully synthesized by sol-gel auto combustion technique using citric acid as a fuel and AR grade metal nitrates. The X-ray diffraction results showed the formation of single phase cubic spinel structure. The crystallite size and lattice constant are in the reported range. The substitution on Zr ions in cobalt ferrite increases lattice constant. The crystallite size confirms the nanocrystalline nature of the samples. The average grain size is found to be in nanometer range and of the order of 16-28 nm. The infrared spectrum shows two absorptions bands in the range $700\text{-}400 \text{ cm}^{-1}$ are the characteristic bands of $\text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$ ferrite revealing the formation of spinel cobalt ferrite. The vibrational bands shows strong influence of zirconium substitution on cobalt ferrite. In summary, the substitution of zirconium ions in cobalt ferrite strongly influences the structural, microstructural and infrared properties.

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Synthesis and Characterizations of Zirconium (Zr⁴⁺) Substituted Cobalt Ferrite (CoFe₂O₄) Nanoparticles Synthesized Via Sol-Gel Auto Combustion Technique

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