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Synthesis of spiral and reverse spiral Co-ferrite by co-precipitation method and XRD Characterization

Muhammad Akmal[1*], Muhammad Mushtaq[2], Munawar Iqbal[2] and Rubab Zahra[1]

[1]*Department of Physics, University of Agriculture, Faisalabd-38040, Pakistan*

[2]*Department of Chemistry & Biochemistry, University of Agriculture, Faisalabd-38040, Pakistan*

Abstract

The Co-ferrite were prepared via co-precipitation of $CoCl_2.6H_2O$, $ZnCl_2.4H_2O$ and $FeCl_3.6H_2O$ salts in the presence of NaOH as a precipitating agent at 90°C. The prepared ferrites were characterized using X-ray diffraction (XRD) and particle size was investigated by sheerer formula. The prepared Co-ferrites were found to be magnetized and particle size was ranged from 22-53 nm. The maximum spontaneous magnetization and minimum particle size was obtained at x = 0.25 when metal ion was in beaker. By reversing the solutions, the ferrites changed from spiral to inverse spiral with decreased particle size. It is found that ferrite properties were dependent to the co-precipitation condition such as concentration of metal ion and solution interchangeability.

Key words: Cobalt ferrite, magnetization, XRD, concentration, spiral and inverse spiral and co-precipitation

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**Corresponding Author*, e-mail: makmaluaf@gmail.com

1. Introduction

Nanomaterials have abundant applications in every field of life such as gas sensors [1], microwave device [2], photo-catalysis [3], adsorption technologies [4], high-frequency transformer technology [5], but currently, magnetic nanoparticles offer widespread applications in biotechnology, such as DNA and RNA purification, cell separation, drug delivery, magnetic resonance imaging [6], magnetic hyperthermia for cancer treatments [7], thermal coagulation therapy, biosensors, biomolecular recognition and cell imaging [8-10]. The soft ferrites are currently used as magnetic cores of transformers, inductors and filters to static power converters [11]. The magnetic properties of the magnetic materials are determined by both intrinsic magnetic and micro structural properties [12-13]. A number of solution-based preparation techniques are available for the preparation of fine particles (which show novel properties when compared to their properties in the bulk) with desirable size and magnetic properties [14]. Very fine ferrite particles can be produced by the chemical co-precipitation and sol–gel methods [15]. Actually, these methods demonstrated that high-density ferrite could be obtained at relatively low sintering temperature, concentration and mixing method [16-18].

In this research work, we used the chemical co-precipitation method for the preparation of Co-Zn ferrite in the presence of NaOH as precipitating agent. The effect of Zn concentration and solution interchangeability on particle size, structural change and magnetization, porosity, bulk properties and lattice constant was studied. The particle size of $CoZnFe_2O_4$ particles prepared from $CoCl_2.4H_2O$, $ZnCl_2$ and $FeCl_3.6H_2O$ was determined by sheerer formula and density, bulk density and-spacing XRD technique.

2. Materials and Methods

The samples of cobalt zinc ferrite ($Co_{1-x}Zn_xFe_2O_4$) powders were prepared by co-precipitation using $CoCl_2.6H_2O$ (cobalt chloride hexahydrated), $ZnCl_2.4H_2O$ (zinc chloride tetra hydrated) and $FeCl_3.6H_2O$ (ferric chloride hexa hydrated) salts. Four samples with varying x (0.25 and 0.50) concentration were prepared (Table 1). The metal chlorides ($CoCl_2.6H_2O$, $ZnCl_2.4H_2O$, $FeCl_3.6H_2O$) and other reagent used for preparation of cobalt zinc ferrite were of analytical grade. For each sample the concentrations of NaOH and $FeCl_3$ were kept constant. All the salts of $CoCl_2.6H_2O$, $ZnCl_2.4H_2O$, $FeCl_3.6H_2O$ with different quantity for different sample were dissolved in the deionized water with minimum volume and then diluted up to 300 mL. In another beaker 200 mL of solution of NaOH was prepared (2M). For sample 1 and 2 the

beaker containing 200 mL solution of NaOH was placed on magnetic stirrer at a moderate stirring speed at room temperature. The beaker containing solution of mixed metallic ions was put into the burette and added it drop wise into the beaker containing NaOH solution on magnetic stirrer until whole the solution was consumed. The stirring speed was gradually increased until precipitation completed. The stirring process stopped and the sample was left to settle down the precipitates for one an hour. For sample 3 and 4, the solutions of beaker and burette were reversed and same procedure was adopted for precipitation. The dark grey precipitates were placed into the pre-heated water bath for digestion. The particles were settled down at the bottom of the beakers after 6 hour. The beakers were taken out of the water bath and cooled at room temperature and filtered. The filtered crystals were washed many times with deionised water to remove free alkali. The precipitates were left to dry at room temperature for 24 hour. The dried particles were homogenized in agitator.

Synthesis route:

$CoCl_2.6H_2O + ZnCl_2.4H_2O + FeCl_3.6H_2O$ ----------> $Co_{(1-x)} Zn_x Fe_2O_4$

Finally, the powder was mixed with binder and put into dye under hydraulic press (10 Kg cm^{-2}). The spontaneous magnetization of pellets was checked for all the samples with permanent magnet. The prepared samples of cobalt zinc ferrites were analyzed with the help of X-ray diffraction technique [19].

The particle size was measured with the width of their diffraction curves [20] whereas X-ray densities were calculated using following formula;

$$d_x = 8M / N_A a^3$$

Where "8" represents the number of molecules in a unit cell of spinel lattice, "M" is molecular weight, "a" is the lattice constant and "N" is the Avogadro's number.

2.1. Statistical analysis

Triplicate sample were prepared and data thus obtained was analyzed statistically to calculate the level of significance of various parameters using analysis of variance technique by Minitab Software Package Version 14.0 (Minitab, Inc., State College, PA, USA) and data were reported as Mean ± SD.

3. Results and discussion

The reaction condition, mixed solution and concentration influence the particle size, shape, and crystallization of the precipitated particles. The effect of Zn and Co concentration and solution interchange on particle size, structural change and magnetization was studied in this work. The effect on the magnetic properties of varying concentration of Zn and solution interchangeability is shown in Table 2 and found that by varying the concentration of Zn and Co has no effect on magnetic effect.

All sample of ferrite prepared by co-precipitation was found to be highly magnetic. Similar results have also been reported by[21] for nano ferrite prepared by co-precipitation method. Fig. 1-4 shows the X-ray diffraction patterns of the precipitated $Co_{(1-x)}Zn_xFe_2O_4$ particles which were prepared at different Co and Zn reacted at various temperatures and their properties are shown in table 2. The XRD pattern data recorded (Table 3) for the sample 1 (Fig 1) in pellet form after a digestion temperature of 90 °C for 6 hours (x=0.25) and metal ion solution in burette indicate characteristic peaks at 2θ values 30.6299°, 35.8883°, 43.4515°, 57.2696° and 62.8358° having Miller indices (2 2 0), (3 1 1), (4 0 0), (3 3 3) and (4 4 0), respectively were observed, which are in close agreement with characteristic peaks of ferrites when compared with ICSD card (with codes 00-001-1121,00-002-1045 and 00-003-0664), which clearly indicates the formation of spinal ferrite of $CoZnFe_2O_4$. Similar, results have also been reported by Mathur *et al*. [22]. The XRD patterns of synthesized sample 2 (Fig 2) shows the characteristic peaks at 2θ values 30.1702°, 35.4916°, 43.0812°, 53.3994°, 56.8609°, 62.4125° and 72.5428° having Miller indices (2 2 0), (3 1 1), (4 0 0), (4 2 2, (3 3 3), (4 4 0) and (5 3 3), respectively, which are in close agreement with characteristic peaks of ferrites when compared with ICSD card (with codes 00-001-1108,00-001-1109 and 00-002-1043). Which are also in good agreement with the reported values by Arulmurugan *et al*. [14].

For sample number 3, the XRD pattern of synthesized sample shows the characteristic peaks at 2θ values 30.5463°, 35.8570°, 43.5327°, 62.8588° and 72.6497° having Miller indices (2 2 0), (3 1 1), (4 0 0), (4 4 0) and (5 3 3), respectively was observed, which are in close agreement with characteristic peaks of ferrites when compared with ICSD card (00-001-1108,00-001-1109 and 00-002-1043), which are in good agreement with the reported values [14]. The sample number 3 was found different because here metal ion solution was taken in burette. Two peaks with maximum intensity were observed, one with relative intensity 87.45 and 100, with 2θ=35.85 and 72.64, respectively. Sample number 4 also showed similar behavior like 3. Overall, the sample number 1 and 2 showed the spinal, while sample 3 and 4 showed inverse spinal structure, which indicate that by inverting the solution from beaker to burette the structure may be inversed. The densities and porosity analysis given in table 4 revealed that x-ray density decreased by increasing Zn concentration in both the cases (metal ion solution in burette and flask). The porosity is the ratio of measured density and X-ray density $P=1-(\rho m/\rho x)$. The average porosity was found to be 0.21-0.25, which is in close agreement with [23]. The effect on lattice constant is shown in fig 5, when the metal ion solution was taken in burette and beaker during co-precipitation at different concentration. The lattice constant was found to be less when metal ion solution was taken in burette as compared to when it was in beaker and NaOH solution in burette at 0.25 x value, while the lattice constant was found greater at 0.50 x value when the metal solution was in burette.

Table 1: Concentrations of $CoCl_2.6H_2O$, $ZnCl_2.4H_20$ and $FeCl_3.6H_2O$ used for the preparation of cobalt zinc ferrite

Sample No.	$FeCl_3$/ 50 mL	$CoCl_2.4H_2O$/ 50ml	$ZnCl_2.4H_2O$/ 50 mL	NaOH/ 100 mL	Temperature 6 hours
1	5.466g	0.640g	2.04g	24g	90 °C
2	5.466g	1.280g	1.18g	24g	90 °C
3	5.466g	1.922 g	0.594g	24g	90 °C
4	5.466g	0.640g	2.04g	24g	90 °C

Table 2: Effect of different concentrations of x (Zn^{+2}) on the spontaneous magnetization of different $Co_{1-x}Zn_xFe_2O_4$ Samples

Sample No.	X	Results
1	0.25	Magnetic
2	0.50	Magnetic
3	0.25	Magnetic
4	0.50	Magnetic

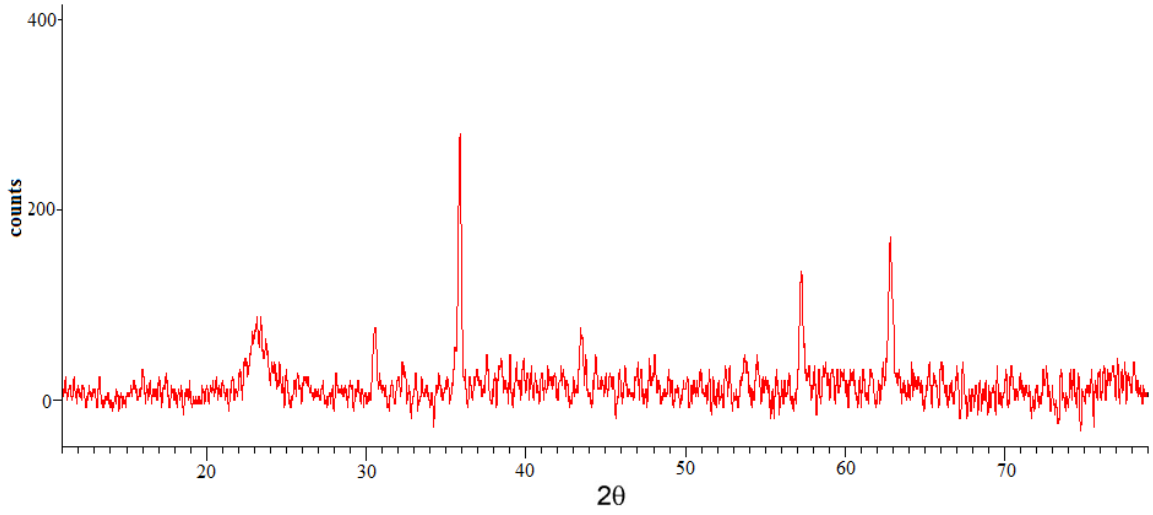

Fig. 1. The XRD pattern of Co-Zn ferrite, sample 1 when x = 0.25 and metal ion solution in beaker

Table 3. Peak Analysis of XRD Pattern of Samples

	Peak No.	Theta (deg)	I/I_0	d-value (A)	hkl	a (A)	r (A)
Sample 1	1	15.31495	23.44	2.91884	220	8.255	2.9186
	2	17.94415	100	2.50231	311	8.299	2.9341
	3	21.72575	21.81	2.08269	400	8.33	2.9451
	4	28.6348	45.64	1.608782	333	8.359	2.9554
	5	31.4179	58.78	1.47772	440	8.359	2.9554
	6	36.1176	64.22	1.25645	533	8.34	2.9455
Sample 2	1	15.0851	27.84	2.96225	220	8.378	2.962
	2	17.7458	100	2.52937	311	8.388	2.965
	3	21.5406	29.9	2.09973	400	8.398	2.969
	4	26.6997	13.4	1.71581	422	8.405	2.971
	5	28.43045	46.39	1.6193	333	8.414	2.974
	6	36.2714	39.18	1.30204	533	8.538	3.018
Sample 3	1	15.27315	26.58	2.92663	220	8.277	2.926
	2	17.9285	87.45	2.50442	311	8.306	2.936
	3	21.76635	33.91	2.07899	400	8.315	2.939
	4	31.4294	55.5	1.47846	440	8.363	2.956
	5	36.32485	100	1.30038	533	8.527	3.014
sample 4	1	15.2865	29.49	2.92414	220	8.27	2.92
	2	17.93525	100	2.50351	311	8.303	2.935
	3	21.7553	21.79	2.08	400	8.32	2.941
	4	31.41335	50	1.47913	440	8.367	2.958
	5	36.2095	100	1.30504	533	8.557	3.025

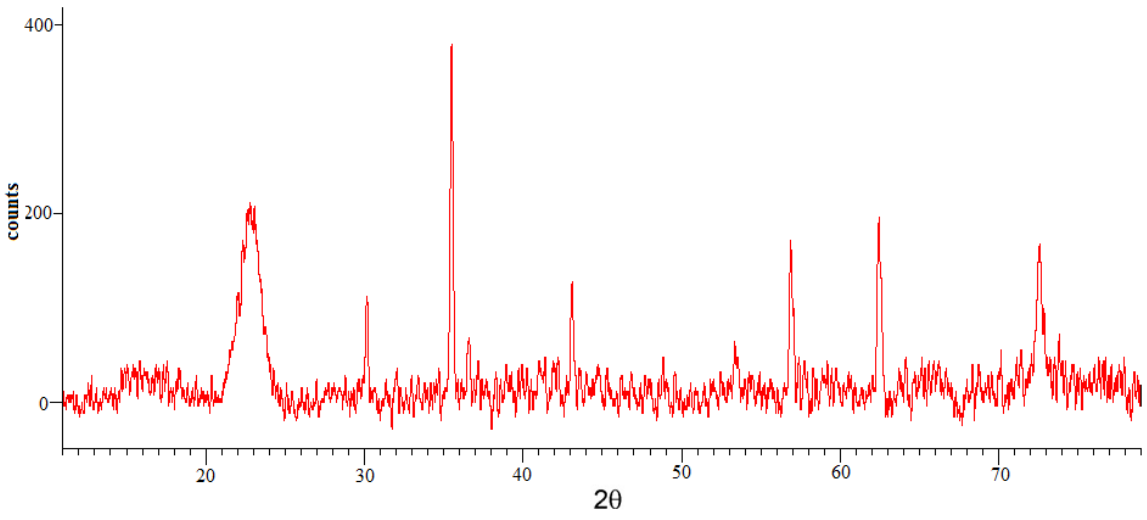

Fig. 2. The XRD pattern of Co-Zn ferrite, sample 2 when x = 0.50 and metal ion solution in beaker

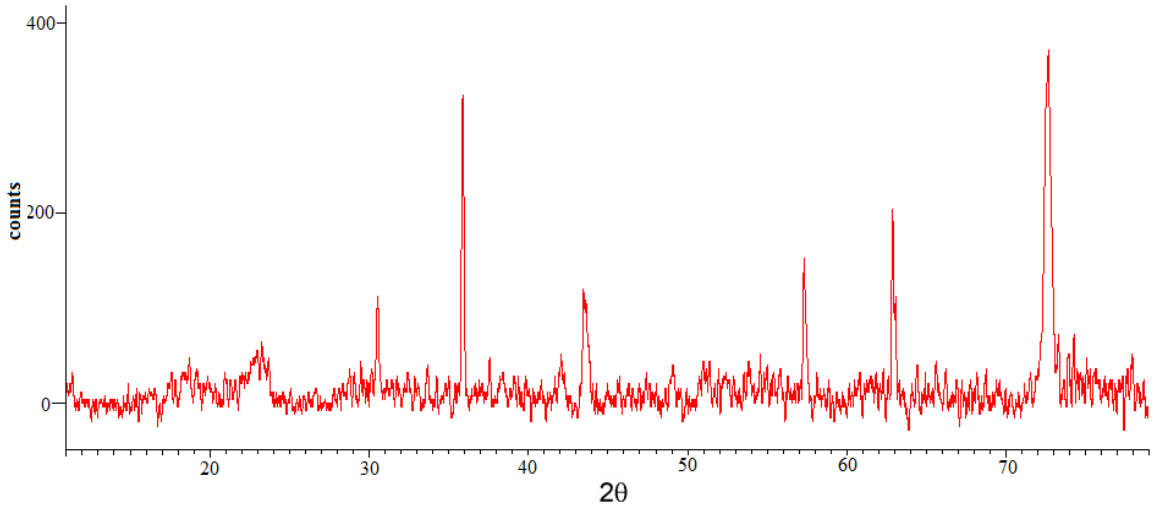

Fig. 3. The XRD pattern of Co-Zn ferrite, sample 3 when x = 0.25 and metal ion solution in burette

Table 4: X-ray Densities and Bulk Densities of the Samples

Sample No.	Concentration(x)	x-ray density	Measured density (g/cm^3)	Porosity
1	0.25	6.921	5.335	0.22
2	0.50	6.68	5.215	0.21
3	0.25	6.833	5.145	0.24
4	0.50	6.820	5.051	0.25

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