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Impurity effect of La on Co ferrite: synthesis and structural study

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Ferrites are most preferable magnetic materials for high frequency applications. Nanomaterials of Co-ferrite and La doped Co – ferrites have been synthesized using co-precipitation technique. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the nanomaterials. Particle size, lattice parameter, strain and dislocation density have been calculated. It has been observed that with La doping strain and dislocation density increases while particle size decreases.

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Keywords: Nanomaterials, Ferrite, Structure

1. Introduction

Nanomaterials of ferrites have many applications, comprising photocatalysis, adsorption technologies, gas sensor, microwave devices and others [1] and the applications of nanoparticles are growing day by day. The market of nanoparticles is billions of dollars [2]. Nanoparticles have wide applications as soft and hard magnetic material for bio, mechanical, electrical and electronic fields [3]. There are different techniques used to synthesize magnetic nanoparticles; the chemical method, mechanical size reduction, gas phase synthesis, thermal hydrolysis, pulse laser deposition, microemulsion, hybrid induction, mechanical chemical processing, HILH method, non-aqueous synthesis, hydrothermal synthesis, plasma torch method etc [2-5] having their own merits and demerits. The properties of ferrites depend on synthesis techniques.

Cobalt ferrites are most preferable magnetic materials due to its low cost, high performance for high frequency applications [6-9]. Cobalt ferrites can be used for high density magnetic recording media. Because of Its properties viz. moderate saturation magnetization, high coercivity, mechanical hardness and chemical stability [10]. Applications of cobalt ferrite can be increase by lanthanum doping. La doped Co ferrite can be used as ferrite rings on computer data cable and magnetic coil to minimize hysteresis loss.

In present work, we have synthesized lanthanum doped cobalt ferrite. XRD and TEM studies are used for characterization of cobalt ferrite and La doped cobalt ferrite. Structural parameters *viz.* particle size, lattice parameter, strain and dislocation density have been calculated.

2. Experimental details

2.1 Materials

Iron (III) chloride anhydrous, cobalt chloride, lanthanum chloride heptahydrate, sodium hydroxide pellets (Merck, AR Grade). All materials were used as received.

2.2 Synthesis

Co-precipitation method was used to prepare cobalt ferrite and La doped cobalt ferrite. Oleic acid was used for formation of nanoparticle to prevent agglomeration [11]. 0.2 M aqueous solution of cobalt chloride and 0.4 M aqueous solution of iron chloride was prepared. Both solutions stirred properly at 40 ^{o}C for half an hour. These solutions were mixed with oleic acid immediately. NaOH was added drop wise till pH becomes 12 - 13.5. The beaker was covered during synthesis to avoid evaporation. Reaction was continued at 100 ^{o}C with proper stirring for 2-3 hrs. The beaker was cooled to room temperature. Precipitates were washed with distilled water 4 to 5 times and then were kept in furnace overnight at 100 ^{o}C. Sample was cooled at room temperature. Magnetic nature of obtained material has been confirmed by bar magnet.

In above process, Reaction might be like below.

$$Co^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow CoFe_2O_4 + 4H_2O$$

The Mechanism of above reaction as follows.

$$Co^{2+} + H_2O \rightarrow Co(OH)_x^{2-x}$$

$$Fe^{3+} + H_2O \rightarrow Fe(OH)_y^{3-y}$$

Overall reaction is

$$Co(OH)_x^{2-x} + Fe(OH)_y^{3-y} \rightarrow CoFe_2O_4$$

$La_xCo_{(1-x)}La_yFe_{(2-y)}O_4$ is general chemical formula used for doping where x = 0.1, y = 0.3. 0.1 M aqueous solution of lanthanum chloride and 0.9 M aqueous solution of cobalt chloride was prepared and mixed at 40 ^oC (solution A). 0.3 M aqueous solution of lanthanum chloride and 0.7 M aqueous solution of Iron (III) chloride was prepared and mixed at same temperature (solution B). Both solution A and B were mixed properly. NaOH was mixed until pH becomes 12 - 13.5. Beaker was covered and kept at 100 ^oC for 3-4 hrs. Precipitate was washed by distilled water and kept sample overnight at 100 ^oC. Bar magnet was used to confirm the magnetic nature of obtained material. The obtained material was then annealed at 450 ^oC for 6 h.

In above Process, Reaction might be like below.

$$xLa^{2+} + (1-x)Co^{2+} + yLa^{3+} + (2-y)Fe^{3+} + 8OH^- \rightarrow La_xCo_{(1-x)}La_yFe_{(2-y)}O_4 + 4H_2O$$

2.3 Characterization

The materials were characterized using X-ray diffraction (Panalytical's X'Pert Pro). The start and end position [in 2θ] were 10.0250 and 79.9750 respectively, having step size [in 2θ] 0.0500. The anode material was Cu. The wavelength of K- alpha is 1.54 Å. The generator was set at 45 kV for 45 mA. Transmission electron microscopy (Hitachi, H-7500, 40-120 kV operating voltage) images of material were obtained at 90 kV.

3. Results and discussions

XRD diffraction pattern of cobalt ferrite and La doped Co ferrite are shown in Fig. 1 and Fig. 2 respectively. Fig. 1 contains six peaks corresponding to (220), (311), (400), (511), (440), (310) planes [12].

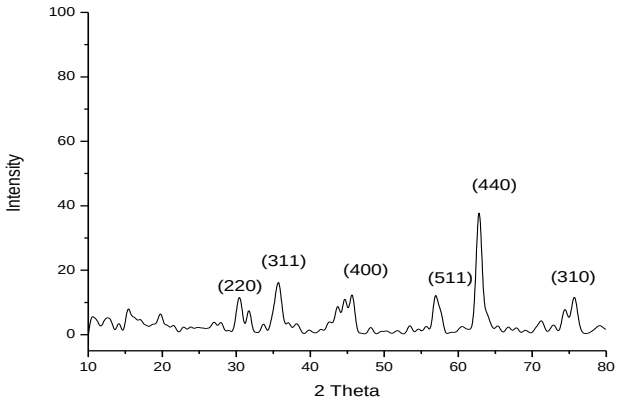

Fig. 1. XRD Pattern of cobalt ferrite.

In La doped Co-ferrite there is a remarkable change in the number of counts (intensity) in XRD data (Fig. 2). Reflection peaks corresponding to (220), (311), (400), (511), (440) and (310) planes [12] are found. Reflection peaks for (220), (400), (511), (310) planes shows an increase in intensity while for (440) plane intensity decreases. The same position of planes in cobalt ferrite and La doped Co ferrite shows homogeneous substitution of Co with La in $CoFe_2O_4$.

XRD spectra have been used to calculate particle size, lattice parameter, strain, and dislocation density. For particle size calculation, Scherrer's formula has been used [13-14],

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

The average particle size of cobalt ferrite and La doped cobalt ferrite was calculated to 52 nm and 50 nm respectively. The atomic size of La is greater than Co. As, La substitute Co, The attraction between La and neighbor atoms may increase due to Vander wall forces, Hence The average size get reduced.

Strain (Є) was calculated using formula [14],

$$\epsilon = \frac{\beta}{4tan\theta} \quad (2)$$

Dislocation density (δ) [14] was calculated using,

$$\delta = \frac{15\epsilon}{aD} \quad (3)$$

Lattice parameter (a) [14] was calculated using,

$$a = d \times \sqrt{h^2 + k^2 + l^2} \quad (4)$$

where, λ is wavelength, θ is Bragg's angle, β is full width half maxima, D is average grain size, ϵ is Strain, d is spacing between two planes. The values of calculated parameters are given in Table 1. Strain of sample increases after doping may be due to decrease in particle size. Dislocation density also increases due to deformation of cubical spinel structure. Lattice parameter increase due to La impurity. This may be due to large atomic radius of La (187 pm) in comparison to Co (125 pm).

Table 1. Values of lattice parameter, strain and dislocation density for cobalt ferrite and La doped cobalt ferrite.

Samples	Particle Size (nm)	Lattice parameter (Å)	Strain	Dislocation density (atom m^{-3})
$CoFe_2O_4$	52	7.099	2.17×10^{-3}	0.8×10^{15}
$La_xCo_{(1-x)}Fe_yCo_{(2-y)}O_4$	50	8.372	2.664×10^{-3}	1×10^{15}

Figs. 3 and 4 shows TEM images of cobalt ferrite and La doped cobalt ferrite respectively. TEM results show an average particle size of 50 nm, supporting our XRD results. Thus, confirming the formation of nanoparticles. An analysis of TEM images shows that there is a change in structure of Co ferrite after La-doping.

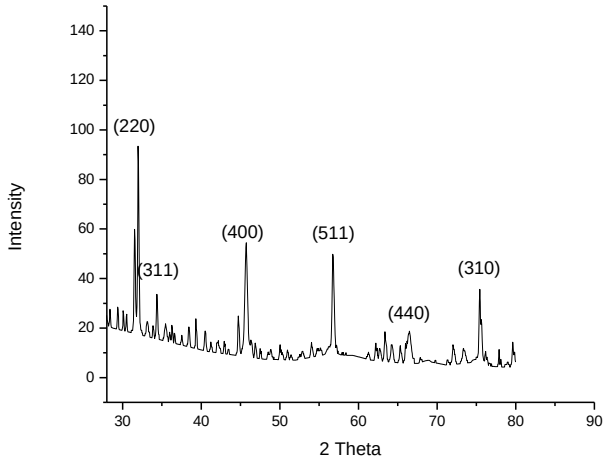

Fig. 2. XRD Pattern of La doped cobalt ferrite.

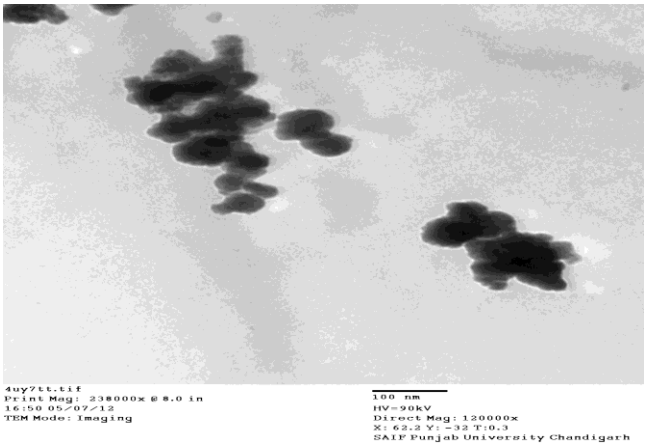

Fig. 3. TEM images of cobalt ferrite.

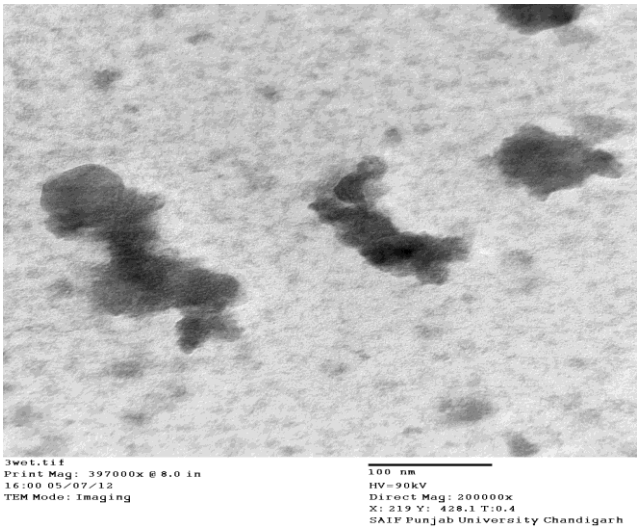

Fig. 4. TEM images of lanthanum doped cobalt ferrite.

4. Conclusion

Co-ferrite and La doped Co – ferrites were successfully synthesized by co-precipitation method. Average particle size for Co-ferrite and La doped Co – ferrites have been found to be 52 nm and 50 nm respectively. Structural results show that with La doping particle size decreases whereas strain, lattice parameter and dislocation density increases. TEM results confirm that the average particle is in accordance with XRD results.

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