Effect of doping Strontium ions in co-precipitated cobalt ferrite

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Abstract. The effect of doping strontium in structural and magnetic properties of co-precipitated strontium cobalt ferrite (Sr$_x$Co$_{1-x}$Fe$_2$O$_4$) nanoparticles are discussed in this paper. The mole of strontium ions was used for doping are 10% of mole cobalt. The synthesis was conducted at a temperature of 95°C with following post annealing at 600°C for five hours. The result of X-ray diffraction showed that the strongest peak intensity of sample decrease when available strontium ions doping. The crystal size decreased from 23.50 to 22.65 nm while the strain increased. The IR spectra of the sample with strontium doping have lower transmittance than the sample without doping. The FTIR result showed that the strontium ions were suppressing the ions in the octahedral site. The magnetic properties showed that coercive field increased and the saturation magnetization decreased with the addition of strontium ions in cobalt ferrite nanoparticles.

1. Introduction
Nano crystallite size of spinel ferrite is the center of attention for researchers in recent years due to their excellent and tuneable (according to the need) electrical and magnetic properties [1]. Among the family of spinel ferrite, cobalt ferrite CoFe$_2$O$_4$ has attracted considerable attention due to their high Curie point (793 K), large magneto crystalline anisotropy, high coercive field, large Kerr effect and Faraday rotation, moderate saturation magnetization, large magnetostrictive coefficient, chemical stability and mechanical hardness [2-7]. These properties, along with their great physical and chemical stability, make CoFe$_2$O$_4$ nanoparticles suitable for magnetic recording applications and new generation electronic devices [8-10].

Pure and bulk cobalt ferrite has inversed spinel structure, where Co$^{2+}$ ions have the preference for the octahedral site (B) while Fe$^{3+}$ ions distribute equally between tetrahedral (A) and octahedral site [11]. The magnetic behavior of this nanoparticle strongly depends on shape, size and the purity of nanoparticles [12]. Magnetic properties of cobalt ferrite strongly depend upon the morphology, and hence greatly influenced by its particle size [13].

Many techniques have been developed for the synthesis of cobalt ferrite nanoparticles during the last year including combustion method [14], hydrothermal [15], thermal decomposition method [16], ball milling [17], sol-gel [18], hot injection thermolysis method [19] and co-precipitation method [10,20,22]. Among the processes, the co-precipitation method has been further developed because of its simplicity, suitable cost, nontoxic precursors, non-time-consuming, and industrial scale yielding...
It is known that the particle size and crystallinity can be controlled by adjusting the super saturation during the nucleation and crystal growth processes, which in turn, can strongly be affected by solution chemistry and precipitation conditions such as reaction temperature and pH of process environment [9-11,20,21].

In this study, we used co-precipitation method to synthesize Sr$_x$Co$_{1-x}$Fe$_2$O$_4$ nanoparticles and focused on investigating the effect of doping strontium in cobalt ferrite. The addition of strontium in cobalt ferrite is expected only to suppress and not substitute ions of cobalt ferrite because of the greater strontium atomic size. In the group of alkaline earth metals, strontium (219 pm) is a better choice in terms of the atomic size because barium (253 pm) has a very large atomic size compared to cobalt (152 pm) and the atomic size of strontium is greater than calcium (194 pm). Strontium substitution will create more strain in lattice site compared to calcium and will create less problem for solid solution compared to barium, variations of mole and annealing temperature are related to stress induce magnetization [1]. The nanoparticles sample characterized by X-ray diffraction (XRD) to analyze the crystal structure and crystallite size, Fourier transform infrared (FTIR) used to analyze the force constant and then vibrating sample magnetometer (VSM) to analyze the magnetic properties.

2. Methods

2.1. Synthesis of Sr$_x$Co$_{1-x}$Fe$_2$O$_4$ nanoparticles

The nanoparticles of Sr$_x$Co$_{1-x}$Fe$_2$O$_4$ (x = 0.0 and 0.1) were synthesized by co-precipitation route as the same previous procedure [23]. The high purity salts Co(NO$_3$)$_2$.6H$_2$O, Sr(NO$_3$)$_2$.6H$_2$O and Fe(NO$_3$)$_3$.9H$_2$O dissolved in 200 ml distilled water under stirring. The synthesis was conducted at a temperature of 95ºC for three hours. The mixed salt solution was added dropwise to the 100 ml 4.8 M NaOH solution under constant stirring. The precipitate washed with ethanol and deionized water. The precipitates were dried overnight at 100ºC to remove excess water. The following variation post annealing has been done at 600ºC for five hours. The precipitates were ground using mortar to obtain fine powder samples. The powder samples were then characterized.

2.2. Characterization

The X-ray diffraction patterns of the samples were recorded with PANalytical X’pert Pro diffractometer using Cu Kα source (1.54 Å) radiation. The lattice constant $a$ was calculated using the following relation:

$$a = \frac{\lambda}{2 \sin \theta} \sqrt{h^2 + k^2 + l^2}$$  \hspace{1cm} (1)

Where $\lambda$ is the wavelength of Cu (Kα), $\theta$ is Bragg’s angle and (hkl) are the Miller indices. The X-ray densities ($d_x$) was determined by the following equation:

$$d_x = \frac{Z M}{N_A a^2}$$  \hspace{1cm} (2)

Where $Z$ is number of molecule per unit cell, $M$ is molecular weight, and $N_A$ is Avogadro’s number [20]. The average crystallite size of Sr$_x$Co$_{1-x}$Fe$_2$O$_4$ nanoparticles of the most prominent peak (311) is determined by using Scherrer’s formula [24]:

$$D = \frac{0.9 / \lambda}{\beta \cos \theta}$$  \hspace{1cm} (3)

Where $\beta$ is the full width at half maximum of the peak. The strain in Sr$_x$Co$_{1-x}$Fe$_2$O$_4$ nanoparticles are determined by using Hall-Williamson plot using the following formula [24]:

$$\varepsilon = \frac{0.9 / \lambda}{\beta \cos \theta}$$
\[ \varepsilon = \frac{\beta_{hkl}}{4 \tan \theta} \] (4)

Where \( \varepsilon \) is the strain and \( \beta_{hkl} \) is the full width at half maximum of the peak.

The IR spectra were recorded in the range of 350-4000 cm\(^{-1}\) by using Shimadzu IR Prestige 21 Fourier transform infrared spectrometer. The force constant for the tetrahedral site \( (k_t) \) and octahedral site \( (k_o) \) was calculated by the following relation [25]:

\[
k_t = 7.62 \times M_1 \times k_1^2 \times 10^{-7} \frac{N}{m}
\]

\[
k_o = 10.62 \times M_2 \times k_2^2 \times 10^{-7} \frac{N}{m}
\] (5) (6)

Where \( M_1 \) and \( M_2 \) are the molecular weight of cations on the A- and B-sites, respectively. The magnetic properties were investigated by using vibrating sample magnetometer Dexing Magnet Ltd type VSM250.

3. Results and Discussion

3.1. Structural analysis

![Figure 1. XRD patterns for Sr\(_x\)Co\(_{1-x}\)Fe\(_2\)O\(_4\) synthesized at temperature of 95°C and annealed at 600°C](image)

The X-ray diffraction patterns of cobalt ferrite without or with doping synthesized by co-precipitation method are shown in Fig. 1. This characterization shows that sample cobalt ferrite without and with doping strontium have a similarity to the data peaks of the International Centre for Diffraction Data (ICDD) number 221086. This similarity signifies that sample cobalt ferrite without or with doping strontium in inverse spinel face center cubic (fcc) structure. The similarity also attributes that there is no other impurities present and the high purity cobalt ferrite without and with doping strontium was successfully produced via co-precipitation method. The strongest peak (311) is located at an angle \( (2\theta) \) 35.63° for sample cobalt ferrite without doping and 35.91° for sample cobalt ferrite with doping strontium. The strontium doping causes the strongest peak angle of cobalt ferrite slightly
shift to the right of 0.28°. The intensity of cobalt ferrite sample decrease with the presence of strontium ions.

| Crystallite size (nm) | x = 0.0 | x = 0.1 |
|-----------------------|---------|---------|
| Lattice parameter (Å) | 23.50   | 22.65   |
| Density (g/cm³)       | 8.34    | 8.28    |
| Strain                | 5.32    | 5.48    |

The crystallite sizes of cobalt ferrite are becoming smaller with the addition of strontium ions are shown in Table 1. The crystallite sizes decrease from 23.50 nm to 22.65 nm with addition strontium ions so the lattice parameter decrease. It causes the density of the nanoparticles cobalt ferrite increase with the addition strontium ions. The strains of cobalt ferrite increase from 0.0048 to 0.0050 with strontium ions doping. This may be because strontium has larger atomic radius than cobalt so that the strontium ions suppress in the cobalt ferrite sample. Kumar et al. report that the lattice strain increase with the addition of strontium ions in SrₓCo₁₋ₓFe₂O₄ sample while the crystallite size decrease.

### 3.2. FTIR analysis

![FTIR spectra](image)

**Figure 2.** FTIR spectra for SrₓCo₁₋ₓFe₂O₄ synthesized at temperature of 95°C and annealed at 600°C

The formation of the spinel structure cobalt ferrite and its cations distribution is supported by FTIR analysis. Figure 2 shows the infrared transmittance spectra of cobalt ferrite sample without and with doping strontium ions. The transmittance of the nanoparticle cobalt ferrite decrease with the addition of strontium ions. The first characteristic absorption band is observed in the wavenumber range of 1500-1400 cm⁻¹ that are thought to derive from the stretching and vibration modes of the H-O-H bending of free or absorbed water molecules [20]. The second characteristic of this absorption band is at wave numbers around 600-400 cm⁻¹ (see inset Fig. 2) which is a common feature of spinel ferrite for both samples. The highest frequency band is located around 600 cm⁻¹ which is regarded as a vibrating stretch of a tetrahedral metal complex consisting of bonds between oxygen ions and metal ions at the
tetrahedral site [20]. Whereas the lower absorption bands located around wavenumber 400 cm\(^{-1}\) are regarded as bending vibrations of octahedral metal complexes consisting of bonds between oxygen ions and metal ions at the octahedral site [20]. This result confirms the appearance of CoFe\(_2\)O\(_4\) in this sample with co-precipitation method.

**Table 2.** FTIR result of sample cobalt ferrite without and with strontium doping

| x     | \(k_1\) (cm\(^{-1}\)) | \(k_2\) (cm\(^{-1}\)) | \(k_t\) (N/m) | \(k_o\) (N/m) |
|-------|----------------------|----------------------|--------------|--------------|
| 0.0   | 590.24               | 393.50               | 14.87        | 10.11        |
| 0.1   | 589.28               | 380.96               | 14.82        | 9.48         |

Table 2 shows that the cobalt ferrite sample force constant at the tetrahedral site has increased from 14.87 to 14.82 N/m in the presence of strontium doping. But with the presence of strontium doping the force constants at the octahedral site decreased from 10.11 to 9.48 N/m. The change of the force constant at the tetrahedral site is 0.05 N/m while the octahedral site is 0.63 N/m. Based on these results, changes in the octahedral site were greater than at the tetrahedral site after doping of strontium ions. So it can be stated that the strontium ions is more pressing on the octahedral site. With the addition of doping ions can decrease and extend the absorption band length of the tetrahedral and octahedral site lattice. This indicates that the frequency difference between tetrahedral and octahedral sites is caused by changes in bond width between the two sites. So the strains that have been calculated in the previous chapter of the sample cobalt ferrite without and with doping strontium ions located at the octahedral site based on the FTIR result.

**3.3. Magnetic properties analysis**

![Figure 3. VSM result for Sr\(_x\)Co\(_{1-x}\)Fe\(_2\)O\(_4\) synthesized at temperature of 95 °C and annealed at 600 °C](image)

Figure 3 shows the hysteresis curve of cobalt ferrite without and with strontium doping synthesized at 95°C and annealed at 600° C for 5 hours. The picture showed that both samples have the same typical hysteresis curve but have different height and width of the curve. It is clear that the sample with strontium doping has shorter and wider hysteresis curves than the sample of cobalt ferrite without
strontium doping. The presence of this strontium doping can affect the magnetic properties of the sample of cobalt ferrite as can be seen in Table 3. Table 3 shows changes in remnant magnetization, saturation magnetization, coercive field and the squareness ratio of the sample cobalt ferrite with addition strontium ions.

| x | \(M_r\) (emu/g) | \(M_s\) (emu/g) | \(H_c\) (kOe) | \(M_r/M_s\) |
|---|---|---|---|---|
| 0.0 | 10.92 | 36.80 | 0.34 | 0.30 |
| 0.1 | 22.98 | 31.32 | 1.07 | 0.73 |

The remnant magnetization of cobalt ferrite samples was seen to increase from 10.92 to 22.98 emu/g with the presence of strontium ions. The presence of strontium ions causing the saturation magnetization of the ferrite cobalt sample decreased from 36.80 to 31.32 emu/g. This decrease in saturation magnetization may be attributed to the cation distribution of the sample. This decrease in saturation magnetization can be identified by the presence of strontium ions occupying site A (tetrahedral) or site B (octahedral). The redistribution of cations in tetrahedral and octahedral is related to the presence strains of force constants in metal bonds in tetrahedral or octahedral results of FTIR characterization. The decrease in saturation magnetization attributed to the strain induced magnetization by breaking the magnetic ion chains with the substitution of non-magnetic ions [1].

The coercive field of the cobalt ferrite sample increased from 0.34 to 1.07 kOe with the addition of strontium doping in the sample. An increased coercive field may be caused by the domain wall pinning on the surface of the nanoparticles [26]. So it can be ascertained that the strontium ions causes the magnetic moment of samples to be difficult to deliver because of the domain wall pinning which then causes the widening of the hysteresis curve from the sample. With a larger coercive field value this cobalt ferrite with strontium doping yields more a square hysteresis curve than sample cobalt ferrite without doping. It can be seen from the squareness ratio value \(\frac{M_r}{M_s}\) of sample cobalt ferrite with doping strontium larger than sample cobalt ferrite without doping. Improvement on coercive field may be influences to the improvement on squarness ratio \(\frac{M_r}{M_s}\). The coercive field indicates the magnetic field required for the demagnetization of the sample. So the cobalt ferrite sample with doping strontium is more difficult to remove the magnetic properties than sample without doping.

4. Conclusion
Cobalt ferrite nanoparticles without and with doping strontium were successfully synthesized using co-precipitation method. The addition of strontium ions in cobalt ferrite causes the crystallite sizes decrease and the strains increase. FTIR result showed that the strontium ions press cobalt ferrite in octahedral site. The magnetic properties showed that the addition strontium ions in cobalt ferrite successfully change the value of remnant magnetization, saturation magnetization, coercive field, and shape of the hysteresis curve.

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