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Lattice strain induced magnetism in substituted nanocrystalline cobalt ferrite

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ABSTRACT

Strontium (Sr) substituted cobalt ferrite i.e. $Co_{1-x}Sr_xFe_2O_4$ ($x=0.00, 0.01, 0.015, 0.02, 0.05, 0.1$) have been synthesized by the citric acid modified sol–gel method. Crystal structure and phase purity have been studied by the X-ray powder diffraction technique. The Rietveld refinement of XRD pattern using the space group $Fd\bar{3}m$ shows monotonically increasing of lattice parameter with the increase in Sr concentration. Magnetic hysteresis loops measurement has been carried out at room temperature using a vibrating sample magnetometer (VSM) over a field range of ± 1.5 T. Magnetocrystalline anisotropy constant were calculated by employing the Law of Approach (LA) to the saturation. It is observed that magnetocrystalline anisotropy has anomaly for $x=0.01$ ($Co_{0.99}Sr_{0.01}Fe_2O_4$) sample. Strain mediated modification of magnetic properties in Sr substituted cobalt ferrite has been observed. The saturation magnetization for doping concentration i.e. $x=0.01$ abruptly increase while for $x>0.01$ decreases with the increase in Sr concentration. A correlation between lattice strain and magnetic behavior in non-magnetic Sr- substituted nano-crystalline cobalt ferrite has been reported.

1. Introduction

Synthesis of magnetic spinel ferrite nanoparticles have remain center of attraction due to their unique properties and numerous potential applications in Ferro fluids technology [1], high density magnetic recording [2], magnetic resonance imaging[3], bio medical drug delivery [4], biosensors [5], biocompatible magnetic nanoparticles for cancer treatment [6] and magneto-optical devices [7] etc. Nanocrystallite size of spinel ferrite is the centre of attention for researchers in recent years due to their excellent and tuneable (according to the need) electrical and magnetic properties. Among the family of spinel ferrite, cobalt ferrite has drawn considerable research interest among the scientific community due to its high coercivity and moderate saturation magnetization with chemical stability and promising mechanical hardness claiming it to be a good candidate for magnetic storage device. Also magnetic properties of cobalt ferrite (CFO) strongly depend upon the morphology, and hence greatly influenced by its particle size [8].

CFO crystallizes in mixed spinel cubic structure with the space group $Fd\bar{3}m$. The mixed spinel structure of cobalt ferrite is represented as $\left[Co_x^{2+}Fe_{1-x}^{3+}\right]\left[Co_{1-x}^{2+}Fe_{1+x}^{3+}\right]O_4$. It has six crystallographic easy axes (directions) along the cube edges of the crystal and four crystallographic hard axes (directions) across the body diagonals denoted as ⟨100⟩ and ⟨111⟩ respectively [9–11].

The property of CFO can be tuned by substituting/doping at Co and/or Fe site. Also, the magnetic properties variation of spinel ferrite by preparing in different methods [12,13] has generated a remarkable research interest in comparative study of magnetic and structural property of spinel ferrite such as $CuFe_2O_4$ [14], $Zn_xCo_{1-x}Fe_2O_4$ [15] and $MgFe_2O_4$ [16].

The tuning of the physical properties of CFO has been addressed by substitution with transition metal, alkali metal, alkaline earth metal, rare earth metal etc. The substitution of cobalt with zinc has been reported to increase the magnetic homogeneity [15], whereas substitution with magnesium yield unusual property like superparamagnetism resulting in the suppression of long range magnetic ordering [17]. There are several reports on different substitution either in Co or in Fe or in both Co and Fe sites of CFO. In all the cases, the magnetic properties depends upon the cationic distribution between tetrahedral and octahedral sites of CFO, strain at lattice sites due to substitution/doping, nature of the substituting/doping element (magnetic or non-magnetic) etc. Out of the above reason, the lattice strain creation in CFO is a centre of attraction by the different researchers. One way to create the lattice strain is by making nanopattern substrate and depositing CFO on it. But it can be only in the thin films. However several researchers have substituted or doped different cations in place of Co and/or Fe in CFO. The maximum strain can be created by substituting larger cations compare to Co and/or Fe. The literature

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survey shows that researchers have tried to substitute or dope different transition elements. There are a few reports on rare-earth element substitutions in Fe site [18,19]. However, most of the cases, the rare earth element does not enter into the lattice site in its bulk form. However, it could be incorporated at the nanocrystalline phase [19]. Also, it cannot incorporate more than 10% as its size is very large compare to Co and Fe. There are a few reports on magnetic rare earth elements substitution in CFO [20–22]. Here the magnetic property is difficult to understand as competition between the magnetism due to substitution of magnetic atom and the magnetism developed by the lattice strain remains unclear.

Alkaline earth metals are non-magnetic. Its substitution at Co site can create strain mediated magnetism in CFO. However preparing these materials is very difficult. In family of alkaline earth metals, Sr is better choice as size (atomic radius) of Ba (253 pm) is very large compare to Co (152 pm) and size of Sr (219 pm) is larger than Ca (194 pm). So it is understood that, Sr substitution will create more strain in lattice site compare to Ca and will create less problem for solid solution compare to Ba. There are a few reports on alkaline earth substituted nanocrystalline CFO [23,24]. However, there is lack of adequate literatures on alkaline earth substituted CFO to understand the crystal structure and magnetic property of these materials. Hence strontium substituted CFO has been prepared by the sol–gel method which is quite economical as well as less cumbersome and time taking technique and, its crystal structure and magnetic property have been reported in the present manuscript. It is observed that, the magnetic parameters are maximum for 1% substitution of Sr in Co site which is due to lattice strain mediated magnetism. The present study opens a window to understand the magnetic properties of cobalt ferrite in terms of strain mediated magnetism.

2. Experimental

2.1. Synthesis of material

$Co_{1-x}Sr_xFe_2O_4$ (x=0.00, 0.01, 0.015, 0.02, 0.05, 0.1) have been synthesized by the citric acid modified sol–gel method using aqueous solution of $Co(NO_3)_2\cdot 6H_2O$, $Fe(NO_3)_3\cdot 9H_2O$ and $Sr(NO_3)_2$ as precursor. The aqueous solution were obtained by dissolving the above chemicals in deionised water (Milli-Q grade, Millipore Corp., Billerica, USA) to produce solutions with $(Co_{1-x}Sr_x)$/Fe mole ratio of 1:2. An aqueous solution of the citric acid was mixed with metal salt solutions. The molar ratio of metal salt solution-to-citric acid was taken as 1:3. The mixed solution was heated at 80 °C with constant stirring using hot plate. The solution became viscous and finally formed brown gel. The gel was dried overnight using an oven at 80 °C in order to remove excess water. During the process of drying, the gel swells into a light and airy mass, eventually broke into brittle flakes. The resulting material was annealed in air atmosphere at 500 °C for 2 h. The chemical reaction involved in the synthesis is as follows:

$$2Fe(NO_3)_3\cdot 9H_2O(aq)+(1-x)Co(NO_3)_2\cdot 6H_2O + xSr(NO_3)_2+3C_6H_8O_7\cdot H_2O(aq)+7/2O_2\rightarrow Co_{1-x}Sr_xFe_2O_4+(39-6x)H_2O+18CO_2+4N_2 \quad (1)$$

2.2. Characterization technique

For the phase purity and structural analysis of annealed sample, X-ray diffraction (XRD) pattern has been recorded using a X-ray diffractometer with CuK_α (1.542 Å) radiation. Williamson–Hall method has been used to determine the particle size and induced strain in the nanoparticles. Rietveld refinements of the XRD patterns have been carried out to deduce the crystal structure parameters. The FE-SEM micrographs have been recorded to study morphology and uniformity in particle size distribution. The magnetic hysteresis was recorded by the Vibrating Sample Magnetometer (VSM) at room temperature with maximum applied field of ± 1.5 T. Law of Approach (LA) to Saturation Magnetization has been studied to deduce the magnetic anisotropy of the synthesized material.

3. Results and discussion

3.1. Structural analysis

X-ray diffraction patterns of $Co_{1-x}Sr_xFe_2O_4$ (x=0.00, 0.01, 0.015, 0.02, 0.05 and 0.1) is shown in the Fig. 1. The patterns show the diffraction lines corresponding to the planes of spinel ferrite. It is evident from the XRD pattern that there is no impurity crystal phase present in the sample i.e. Sr^{2+} has been incorporated into the lattice site and the material exist in single crystal phase within the XRD limit. The crystallite size has been calculated using Williamson Hall (WH) formula [25];

$$\beta\ \cos(\theta) = \frac{0.9\lambda}{D} + 4\epsilon\ \sin(\theta) \quad (2)$$

Where β is full width at half maxima (FWHM), θ is the Bragg's angle, λ is the wavelength of used X-ray, D is the crystallite size and ε represents the intrinsic strain. The typical Williamson Hall plots ($4\sin(\theta)$ versus $\beta\cos(\theta)$), are shown in the Fig. 2 for $Co_{0.99}Sr_{0.01}Fe_2O_4$ and $Co_{0.98}Sr_{0.02}Fe_2O_4$. The crystallite sizes are enlisted in Table 1 for all the samples. The crystallite size decreases monotonically with increasing strontium concentration. It is because the ionic radius of Sr^{2+} (132 pm) is larger than the ionic radius of Co^{2+} (88.5 pm) ion, and when Co^{2+} is replaced with Sr^{2+}, it produces lattice strain which hinders the crystal growth. However, the crystallite size lies in a narrow of 18–8 nm i.e. ± 5 nm. This narrow size distribution is taken care during preparation.

All the XRD patterns obtained were analyzed by the Rietveld refinement technique with the help of fullprof program 2011. The expression used in the Rietveld method is defined as [26]:

$$FWHM^2 = (U + D_{ST}^2)(\tan^2\theta) + V\ \tan(\theta) + W + \frac{IG}{\cos^2\theta} \quad (3)$$

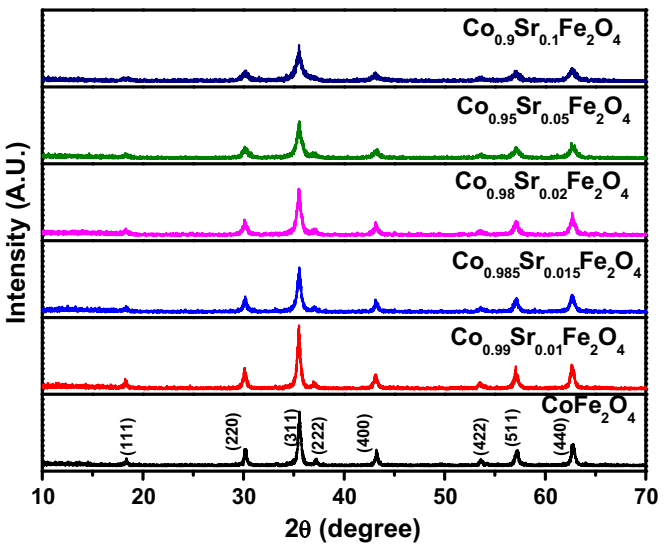

Fig. 1. XRD Patterns of $Co_{1-x}Sr_xFe_2O_4$ for x= 0, 0.01, 0.015, 0.02, 0.05 and 0.10.