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Correlation between lattice strain and magnetic behavior in non-magnetic Ca substituted nano-crystalline cobalt ferrite

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Abstract

Magnetic nanoparticles of calcium (Ca)-substituted cobalt ferrite i.e. $Co_{1-x}Ca_xFe_2O_4$ ($x=0.00$, 0.01, 0.015, 0.02, 0.05, 0.1, and 0.15) have been synthesized by the citric acid modified sol–gel method. X-ray powder diffraction (XRD)patterns confirm the formation of spinel phase. The particle size decreases with the Ca concentration. The Rietveld refinement of XRD patterns using the space group – $Fd\bar{3}m$ shows monotonically increasing of lattice parameter with the increasing concentration of Ca. The FT-IR spectrum recorded in the range of 325–1000 cm^{-1} and Raman spectrum obtained in the range of 88–800 cm^{-1} shows the formation of spinel phase belonging to $Fd\bar{3}m$ space group supporting structural analysis from XRD patterns. Magnetocrystalline anisotropy has been obtained using "Law of Approach (LA) to Saturation magnetization". Saturation magnetization and remnant magnetization is maximum for 1% Ca substitution which could be due to strain mediated magnetism. However these magnetic properties decrease with the Ca substitution for the percentage above 1%. It could be due to decrease of magnetic exchange interaction in the sample. A correlation between magnetic behavior and lattice strain has been established in non-magnetic Ca substituted nano-crystalline cobalt ferrite. In order to investigate the ferromagnetic nature of the sample, Arrott plot analysis has been carried out. Difference in saturation magnetization obtained from LA to saturation and Arrott plot analysis gives the qualitative information about the influence of lattice strain on saturation magnetization.

Keywords: Spinel ferrite; Magnetocrystalline anisotropy; Rietveld; Arrott plot

1. Introduction

Due to novel magnetic property like spin canting and superparamagnetism, single domain nanoparticle has attracted much attention in scientific community in recent years. Among them spinel ferrite has drawn considerable attention. Cobalt ferrite (CFO) is one of the well-studied materials among Spinel ferrite. Research on spinel ferrite dated back to several decades. Magnetic property of CFO depends upon several factors like cobalt content, sample preparation, particle size and shape among others. It is ferrimagnetic in bulk and crystallizes in mixed spinel phase with space group $Fd\bar{3}m$ having general formula $\left(Co_x^{2+}Fe_{1-x}^{3+}\right)\ \left[Co_{1-x}^{2+}Fe_{1+x}^{3+}\right]O_4$ [1]. Round and square brackets corresponds to tetrahedral (A site) and octahedral (B site) sites respectively. If $x=1$, then structure is normal structure and for $x=0$, structure is inverse spinel structure otherwise structure is in mixed spinel structure. The unit cell of CFO consists of 64 tetrahedral sites and 32 octahedral sites. Out of these 8 tetrahedral and 16 octahedral sites are occupied by metal ions. It has been also shown that annealing of the cobalt ferrite can also be used to alter the ion concentration at octahedral and tetrahedral sites [2,3]. CFO has also attracted attention due to its interesting magnetic properties like moderate saturation magnetization, high coercivity and Curie temperature (around 790 K) having good mechanical hardness and chemical stability [4]. It exhibits high cubic magnetocrystalline anisotropy which is the common feature of spinel ferrite [5]. Due to these features, nanocrystalline cobalt ferrite can be used for various technological applications like microwave, ferrofluid technology, high density magnetic storage device, etc. [6]. Therefore from technological point

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of view, it is important to understand and modify the magnetic properties according to the requirement. 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 [7–9]. CFO provides large window for the physical property modification as its property can be modified with doping as well as synthesis process.

Several efforts have been madeby the several researchers to modify the magnetic property of CFO by doping with transition element, post transition element as well as rare earth element. $Co_{0.2}Zn_{0.8}Fe_2O_4$ synthesized by the co-precipitation method shows decrease in magnetization with increasing particle size [10] followed by Arulmurugan et al. [11] observation that substitution of Co^{2+} with Zn^{2+} lead to improvement in magnetic properties of nanocrystalline ferrites with decreasing behavior of saturation magnetization and the particle size of ferrite nanoparticles with increasing Zn concentration. Sonal et al. [12] synthesized $Co_xZn_{1-x}Fe_2O_4$ ($x=0.0$–1.0) via sol–gel method with an interesting observation of increasing saturation magnetization upto $x=0.4$ and decreasing afterwards. They suggested such type of behavior might be due to variation of exchange interaction between the tetrahedral and the octahedral sites. Ranvah et al. [13] studied temperature dependence of magnetic anisotropy of Ga substituted CFO. They found that magnetic anisotropy increases with decreasing temperature and decreases with increasing Ga content at all temperature. They also observed increased value of anisotropy at 10 K for 10% and 20% Ga substitution at iron site suggesting that it may be due to more favorable occupancy of Ga at tetrahedral site and further decrement of anisotropy with increasing substitution may be due to noncollinear spin arrangements brought on by the decreased tetrahedral–octahedral exchange coupling. This will require further investigation. There are other reports [14–17] available on modification of magnetic properties of CFO by different ways.

The magnetic properties can be modified by creating lattice strain in CFO. 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 and would not be economical for many applications. Strain in CFO lattice has been created by substituting Ca ion in place of Co ion in CFO. This has been done by economical synthesis method (citric acid modified sol–gel method).There are a few reports on Ca substituted CFO in their bulk form [18–19]. Also, as per best of our knowledge, a report is available on nanoparticle size of Ca doped CFO [20]. Magnetic properties and AC conductivity of the material has been discussed by Saafan et al. [20]. AC conductivity is found to increase with Ca substitution. Magnetic properties have shown anomaly for 1% and 7% substitution but there is no detailed analysis of Magnetic behavior to understand the interesting properties on this substitution. In this report, the magnetic behavior of $Co_{1-x}Ca_xFe_2O_4$ ($x=0.00$, 0.01, 0.015, 0.02, 0.05, 0.1, and 0.15) has been studied extensively by employing LA to saturation and its co-relation with lattice strain is reported. Also Arrott plot analysis has been deployed to extend the understanding of magnetic behavior. Hence, the present article enlarges the window for understanding and modification of magnetic properties of CFO which can extend its applications.

2. Experimental

2.1. Synthesis of material

$Co_{1-x}Ca_xFe_2O_4$ ($x=0.00$, 0.01, 0.015, 0.02, 0.05, 0.1, and 0.15) 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 $Ca(Co_3)_2$ as precursor. The aqueous solution of these chemicals were produced by dissolving these chemicals in deionized water (Milli-Q grade, Millipore Corp., Billerica, USA) to produce solutions with $(Co_{1-x}Ca_x)$/Fe mole ratio of 1:2. An aqueous solution of 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 550 °C for 2 h.

2.2. Characterization technique

For the phase purity and structural analysis of annealed sample, X-ray diffraction (XRD) patterns have been recorded using an X-ray diffractometer (Rigaku TTRX lll 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. The Rietveld refinement of the XRD patterns have been done to deduce the lattice parameter using FullProf 2011 program. To study the molecular dynamics FTIR spectrum and Raman Spectrum has been recorded. Raman spectra were recorded within the wave number range 88–800 cm^{-1}in the backscattering geometry using confocal Micro-Raman Spectrometer (Seki Technotron Corporation, Japan) with 514 nm Argon ion LASER as excitation source by STR Raman Spectrograph. A 100× microscope was used to focus the LASER beam and collect the light. FT-IR was recorded with a PerkinElmer (Model Spectrum 400) within the wave number range of 325–1000 cm^{-1}. The magnetic hysteresis loop was recorded by Lakeshore (Model no. 7410) Vibrating Sample Magnetometer (VSM) at room temperature in maximum applied field of ± 1.4 T.

3. Result and discussion

3.1. XRD

XRD patterns of $Co_{1-x}Ca_xFe_2O_4$ ($x=0.00$, 0.01, 0.015, 0.02, 0.05, 0.10 and 0.15) synthesized by modified citric acid method is shown in the Fig. 1. The pattern shows the phase purity of synthesized material. The spectrum confirms the

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