Advanced Powder Technology 26 (2015) 213–223

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Structural and magnetic properties of nanocrystalline yttrium substituted cobalt ferrite synthesized by the citrate precursor technique

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ARTICLE INFO

Article history:
Received 30 July 2014
Received in revised form 23 September 2014
Accepted 1 October 2014
Available online 29 October 2014

Keywords:
X-ray diffraction
Raman spectroscopy
Magnetocrystalline
Coercivity
Magnetization

ABSTRACT

$CoFe_{2-x}Y_xO_4$ ($x = 0.0$ and 0.05) compound has been synthesized by citrate precursor method and, their structural and magnetic properties have been investigated. X-ray diffraction and Raman spectroscopy have been used to confirm the formation of single phase cubic spinel structure. The X-ray diffraction patterns have been analyzed employing Rietveld refinement technique. The surface morphology and particle size of the samples have been examined using FE-SEM and TEM. Substituting small amount of Y^{3+} cation causes significant reduction of the particle size. The magnetic hysteresis curve recorded at room temperature using VSM over a field range of ±2 T shows enhancement in coercivity and reduction in highest magnetization with the Y^{3+} substitution. The enhancement of coercivity is attributed to the transition from multidomain to single domain state. The cubic magnetocrystalline anisotropy constants for present samples has been determined by "law of approach" to saturation which suggests the smaller value for substituted sample ($x = 0.05$) than that of unsubstituted sample ($x = 0.0$). ZFC and FC magnetization measurement over the temperature range 300–900 K shows blocking temperature is far above than room temperature. The decrease of highest magnetization and magnetocrystalline anisotropy constant is ascribed to weakening of superexchange interaction and surface effect.

1. Introduction

Cobalt ferrite ($CoFe_2O_4$) is a centrosymmetric hard magnetic material which crystallizes to $Fd\bar{3}m$ space group with cubic mixed spinel structure. This compound is represented as $\left(Co^{2+}_{\delta}Fe^{3+}_{1-\delta}\right)\left[Co^{2+}_{1-\delta}Fe^{3+}_{1+\delta}\right]O_4$, where cations inside the round and square brackets occupy A-sites and B-sites respectively, and δ (degree of inversion) depends on thermal history and preparation condition [1,2]. Its magnetic ordering temperature is around 520 °C, which is far above than room temperature. It exhibits high coercivity, large magnetocrystalline anisotropy, moderate saturation magnetization, and, excellent chemical, thermal and structural stability at room temperature [3,4]. Hence, this material is a promising candidate for a wide variety of technological applications at room temperature such as drug delivery, magnetic sensors, actuators, memory and high frequency devices [5,6]. The magnetic behavior in this material is governed by the spin coupling of the unpaired 3*d* electrons of Co^{2+} and Fe^{3+} cations present at the A and B-sites. Hence, various superexchange interactions exits inside the structure such as Fe^{3+}(B)–O–Fe^{3+}(B), Fe^{3+}(B)–O–Co^{2+}(B), Fe^{3+}(B)–O–Fe^{3+}(A), Co^{2+}(B)–O–Fe^{3+}(A) and Co^{2+}(A)–O–Fe^{3+}(B) which is responsible for magnetic behavior in this compound. Among these superexchange interactions, the interaction between A and B site is the strongest one which mainly controls the magnetic behavior of the cobalt ferrite [7–9]. The physical properties of cobalt ferrite nanoparticles depend upon its size and composition. One could tune the size of the cobalt ferrite nanoparticle by tailoring its chemical composition in order to get the modified properties. However, it is difficult to tune the size of the particle in control way as the size is affected by the rate of the nucleation and its subsequent growth. The size of the particle can be controlled by restricting particle's rate of the nucleation and its subsequent growth with introducing a large strain at the lattice site by incorporating suitable substituent element [10–12]. Rare earth elements (La^{3+}, Gd^{3+}, Sm^{3+}, Y^{3+} etc.) have larger ionic size than that of Fe and Co ions. Substituting very small amount of rare earth cations at the Co and/or Fe site will create a large strain at the lattice site which may restrict the rate of the nucleation of the particle and its subsequent growth. Several authors have reported the synthesis of rare earth cations substituted cobalt ferrite by solid state

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http://dx.doi.org/10.1016/j.apt.2014.10.002
0921-8831/

route and chemical method. However, it suffers from drawbacks like phase segregation of metal monoxides, hematite and orthoferrites even for very low concentration of rare earth cations substitution [13–15]. A few reports are available which have mentioned the synthesis of rare earth substituted nanocrystalline spinel ferrites in single phase form using chemical route despite having big difference in ionic radius of rare earth cations and Co/Fe cations [16–22]. The magnetic behavior in RE^{3+} (RE: rare earth) element is due to 4*f* electrons. Hence substituting small amount of Y^{3+} cations in Place of Fe ions, one can expect an appearance of spin coupling of 3*d*-4*f* electrons, which will modify the physical properties. Hence the present report is aimed to synthesis the single phase yttrium (Y^{3+}) cations substituted cobalt ferrite using chemical route and investigates its structural and magnetic properties.

2. Experimental

Yttrium (Y^{3+}) substituted cobalt ferrite compound with empirical formula ($CoFe_{2-x}Y_xO_4$, $x = 0.0$ and 0.05) have been synthesized by the citrate-precursor method. Cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), Iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), Yttrium oxide (Y_2O_3) and citric acid ($C_6H_8O_7{\cdot}H_2O$) supplied with 99.9% purity were used as starting materials. The clear solution of yttrium nitrate was obtained by dissolving Yttrium oxide in nitric acid. The aqueous solution of cobalt nitrate, iron nitrate and citric acid were obtained by dissolving it in deionized water. An aqueous solution of citric acid was mixed with the above metal nitrates solutions. The mixed solution was kept on a hot plate with a continuous stirring at 90 °C. The citric acid plays two important roles: on one hand, it provides fuel for the reaction, as decomposition of citric acid in the solution liberates heat (exothermic process) which implies that the heat required for chemical reaction is provided by the reaction itself. On the other hand, it has an ability to form complexes with metal ions. Thus, citric acid acts as a ligand to stabilize metal ions. Generally the molar ratio of citric acid to metal nitrates is maintained high to form a cage like linkage so that metal ions are no longer free to undergo many of its chemical reaction to produce precipitates. In the present work, the molar ratio of metal nitrates to citric acid was taken as 1:3. The mixture solution became viscous during evaporation. This viscous gel was dried in a heating oven at 100 °C for 10 h in order to remove excess water. After that it was heat treated in air atmosphere at 200 °C for 1 h to produce deep brown colored ashes. The ashes were grinded and annealed at 800 °C for 2 h. The annealing temperature 800 °C was selected after the TGA analysis.

Thermogravimetric analysis (TGA) of the samples were carried out using PerkinElmer STA 6000 instrument in the nitrogen atmosphere under the heating rate of 10 °C/min. Powder X-ray diffraction pattern at room temperature were recorded by rotating anode based Rigaku (TTRX-III) X-ray diffractometer operating at 50 kV and 100 mA in order to examine the crystalline phase of the annealed samples. The measurements were performed using the Cu Kα radiation ($\lambda = 0.154$ nm). The structural analysis by the Rietveld method has been carried out using FullProf suite. The composition of the sample was studied by EDS (Energy-dispersive spectroscopy) using the Hitachi S4800 Field Emission Scanning Electron Microscopy (FE-SEM). The particle size measurement were carried out by transmission electron microscopy (TEM,) using the JEM-2100 JEOL device. Raman spectra were measured in the backscattering geometry using confocal micro-Raman spectrometer (Seki Technotron Corp Japan) with the 514.5 nm laser line as excitation source by STR 750 RAMAN spectrograph. A 100× microscope was used to focus the laser beam and collects the scattered light. Magnetic hysteresis loops were measured at room temperature by using a Lake Shore (Model No. 7410) Vibrating Sample Magnetometer (VSM) over a field range of ±2 T. ZFC and FC magnetization measurement were carried out at 100 Oe magnetic field over the temperature range 300–900 K using VSM insert of Physical Properties Measurement System (PPMS) of quantum design.

3. Results and discussion

3.1. Thermogravimetric analysis (TGA)

Typical TGA curve of the as synthesized sample of $CoFe_{1.95}Y_{0.05}O_4$ is shown in Fig. 1. The TGA curve shows gradual and continuous weight loss of about 9% between 100 and 700 °C. The analysis of the above TGA curve has been carried out within the temperature range 90–200 °C, 200–750 °C and 750–1000 °C respectively. As prepared sample consists of hydroxyl group, carboxyl group and nitrate ions. There is a weight loss of about 5% within the temperature range 90–200 °C, which is ascribed to evaporation of the residual water content from the sample. The weight loss of about 4% is observed between 200 and 750 °C which corresponds to decomposition of metal nitrates into the corresponding oxides and removal of the residual organic components. No further weight loss has been observed for the temperature higher than 750 °C, which indicates that sample is free of residual reactants and carbonaceous matter. It confirms that stable spinel ferrite phase of $CoFe_{1.95}Y_{0.05}O_4$ has been formed above 750 °C.

We have selected 800 °C as annealing temperature in order to get a well crystallized phase following the above thermal analysis result. It has also been reported that formation of rare earth cations such as Sm^{3+} substituted cobalt ferrite sample in nanocrystalline form starts after annealing at $\geqslant$400 °C [22]. The above TGA pattern shows small weight loss of about 0.6% between 400 and 750 °C for $CoFe_{1.95}Y_{0.05}O_4$. Hence we also annealed the samples at 450, 600 and 750 °C and recorded the XRD pattern of these annealed samples. The XRD pattern of the $CoFe_{1.95}Y_{0.05}O_4$ sample annealed at 450 °C show broader peaks in comparison to unsubstituted sample (figure not shown). It is due to presence of high strain at the lattice site which leads to incomplete crystallization of the Y^{3+} substituted sample in comparison to unsubstituted sample. It reveals that, thermal energy for 450 °C annealed samples is not sufficient for the incorporation of the Y^{3+} ions into the spinel lattice due to large difference in ionic radius of Y^{3+}(0.91 Å) and Fe^{3+}(0.64 Å) cations. Therefore more energy is needed to make Y^{3+} cations enter into the spinel lattice to complete the crystallization. The XRD pattern of the samples annealed at 750 °C shows significant reduction in the peak broadening with well resolved diffraction peaks compare to that of samples annealed below 750 °C. It suggests that sample $CoFe_{1.95}Y_{0.05}O_4$ is well crystallized into spinel phase crystals with reduction in internal strain. Based on above observation, the samples were annealed above than 750 °C in order to get a well crystallized phase which was used for further characterization.

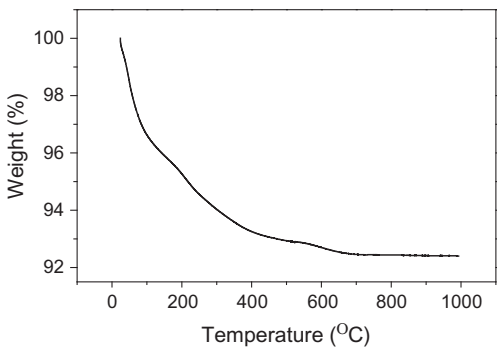

Fig. 1. TGA curve of as prepared $CoFe_{1.95}Y_{0.05}O_4$.