Journal of Magnetism and Magnetic Materials 461 (2018) 69–75

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Research articles

Effect of yttrium doping on structure, magnetic and electrical properties of nanocrystalline cobalt ferrite

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ARTICLE INFO

Article history:
Received 18 January 2018
Received in revised form 23 March 2018
Accepted 23 April 2018
Available online 25 April 2018

Keywords:
Nanostructures
Rietveld analysis
Infrared spectroscopy
Crystal structure and microstructure
Ionic conductivity

ABSTRACT

Tailoring of properties by changing morphology or by doping is very much required for the suitable application of any materials. Here we report the effect of yttrium doping on microstructure, magnetic and electrical properties of cobalt ferrite nanoparticles prepared through citrate auto-ignition method. Rietveld refinement analysis of X-ray diffraction pattern confirms the growth of pure and single phase cobalt ferrite nanoparticles which corroborates with transmission electron microscopy (TEM) study. Microstructural parameters, obtained from Rietveld analysis showed that oxygen vacancy is maximum and inter-ionic bond lengths and bond angles attain optimum values for 15 mol% yttrium doped sample. An observed value of saturation magnetization indicates the existence of spin canting phenomenon which was explained by Yafet-Kittel model. Magnetic parameters such as anisotropy constant, anisotropy field have been estimated using Law of Approach (L.A.) formalism. Existence of interparticle dipolar interaction (IPDI) in the system was established with the help of M_r/M_s ratio around room temperature. Maximum electrical conductivity has been observed for the 15 mol% doped sample as estimated from Mott's 3-D V.R.H. model, which can be attributed to the optimum values of microstructural parameters at this composition.

1. Introduction

Tremendous interest on science and technology of nanomaterials is strongly motivated by the idea that it can change all most all the physical and chemical properties drastically while comparing with bulk their counterpart. Nanocrystalline spinel ferrites are being largely explored for their application in various devices. In particular, cobalt ferrite nanoparticles have attracted increasing interest due to their applicability in high density magnetic recording, magnetic resonance imaging (MRI), drug deliver, gas sensing and various other fields.

Efforts have been made to tailor the properties of nanocrystalline cobalt ferrites either by doping or making composites. Cr^{3+} substituted cobalt ferrite nanoparticles have been explored to increase the coercivity for effective use in high density magnetic recording [1]. Cobalt ferrite-Graphene oxide nanocomposite was investigated successfully for the use of MRI and controlled drug delivery purposes [2,3]. Talukdar et al. has reported photoluminescence and photocatalytic activities for cobalt ferrite nano-hollow spheres [4]. Influence of cobalt ferrite nanoparticles in cell transcription and alteration of cell phenotype was reported by Gharibshahian [5]. Gas sensing properties of cobalt ferrite nanoparticles has been demonstrated by Joshi et al. [6]. In addition, environmental applications of cobalt ferrite nanoparticles were also enlightened successfully by Hu et al. [7]. Altogether, cobalt ferrite is an important material which has application potential in various fields.

Crystallographic structure plays an important role in controlling the chemical and physical properties of any materials. So, detail investigations on the structure of materials are quite meaningful to interpret different changes in the properties of the material. Spinel ferrites contain two sub-lattices which are called tetrahedral [A] and octahedral [B] site respectively [8,9]. Normally cobalt ferrite exhibits inverse spinel structure in its bulk form. Reduction of grain size to nanometer range promotes the formation of mixed spinel structure due to the change in distribution of cations over two interstitial sites. Co and Fe, both are being 3d block element, can reside in multivalent states and can be easily doped with other cations to made changes in the ultimate electronic configuration, magnetic, transport and other properties of the material [10–12]. Also change in preparatory conditions and different growth techniques can create various kinds of defects in crystals, can affect

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https://doi.org/10.1016/j.jmmm.2018.04.051
0304-8853/

Table 1
Sample code names.

Sample abbreviation	Sample formulation
Y0	$CoFe_2O_4$
Y10	$CoFe_{1.9}Y_{0.1}O_4$
Y15	$CoFe_{1.85}Y_{0.15}O_4$
Y20	$CoFe_{1.8}Y_{0.2}O_4$
Y30	$CoFe_{1.7}Y_{0.3}O_4$

the size of grain and grain boundaries which in turn will be reflected on the properties of the material.

Changes in different physical and chemical properties by doping with various rare earth ions in cobalt ferrite nanoparticles has recently been studied by several research groups [8,13–18]. Different synthesis procedures have been adopted to prepare single phase RE doped cobalt ferrite nanoparticles. The increase in coercive force by doping with Gd^{3+}, Tb^{3+} and Dy^{3+} ions [13], Nd ion [14], increase of anisotropy properties due doping by Dy ion [8] in cobalt ferrite has been reported earlier. Again decrease in saturation magnetization and coercivity of cobalt ferrite nanoparticles by Dy substitution was reported by Kambale et al. [15]. Strong L–S coupling from the Co^{2+} ions in the octahedral lattice [16], appearance of secondary phases at higher sintering temperature and their influence on magnetic properties have also been reported [17,18].

Here we have systematically studied the effect of yttrium doping on the structure, electrical and magnetic properties of nanocrystalline cobalt ferrite. Single phase Y doped cobalt ferrite, $CoY_xFe_{1-x}O_{4\pm\delta}$ NPs were prepared up to 30 mol% (x = 0, 0.1, 0.15, 0.2, 0.3) while to the best of our knowledge, previous report claimed it can go up to maximum 20 mol% [18]. Rietveld analysis of XRD data also confirmed the absence of any impurity. Microstructural analysis have been performed and a structure-property correlation is established to accommodate the effect of Y^{3+}doping on magnetic and ionic properties of system.

2. Experimental

2.1. Sample preparation

Nanocrystalline $CoY_xFe_{1-x}O_{4\pm\delta}$(x = 0, 0.1, 0.15, 0.2, 0.3) were prepared through the low temperature citrate auto-ignition method. $Co(NO_3)_2$, Y_2O_3, $Fe(NO_3)_2$ and citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$) were used as precursors for the preparation. All materials were purchased from Sigma-Aldrich and utilized without further purification. Y_2O_3 was mixed with de-ionized water and nitric acid and stirred at 60–65 °C using magnetic stirrer for 2 h to prepare yttrium nitrate. Then stoichiometric amounts of Co $(NO_3)_2$ and $Fe(NO_3)_2$ were mixed with the solution. Citric acid was added at 3:1 M ratio. The entire solution was stirred for 8 h at temperature 80–85 °C. When the gel was formed, whole beaker was taken into a furnace and heated around 120 °C to complete the auto-ignition process. Ashes thus formed, grounded in an agate mortar to get the powder sample. Powder samples was then sintered at 800 °C for 2 h for further experiments.

Series of samples of different yttrium concentration have been prepared and listed in Table 1 with their code names and corresponding formulae.

2.2. Sample characterization

Powder diffraction pattern of the prepared samples in 2θ range from 20° to 90° was record with X-Pert Pro X-ray diffractometer (PANLYTICAL, Almelo, The Netherlands) fitted with nickel filter

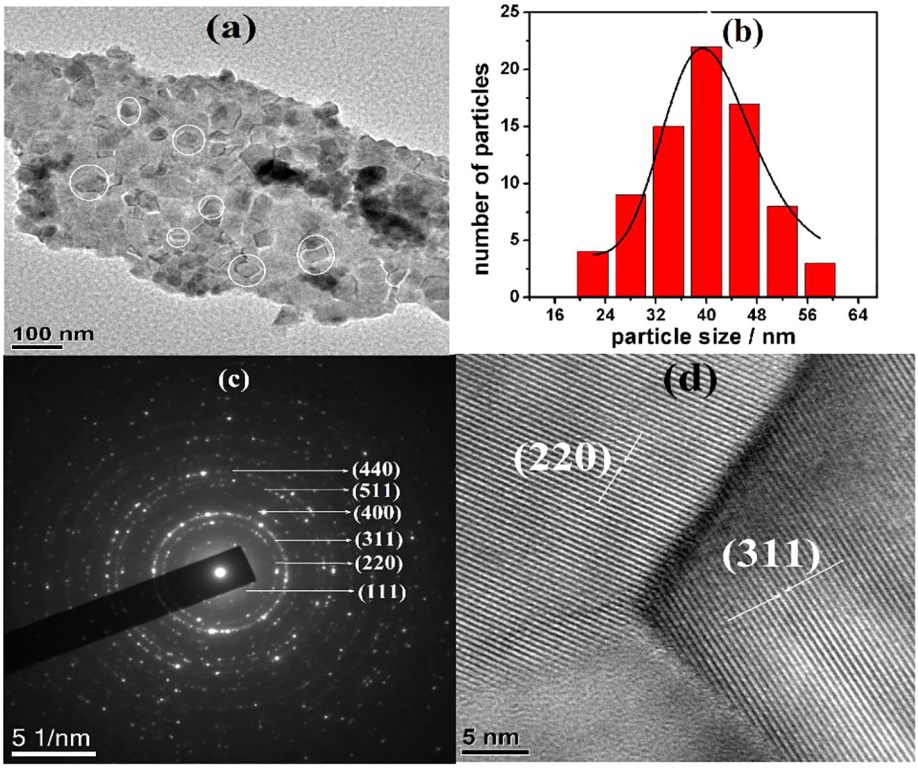

Fig. 1. (a) TEM micrograph, (b) particle size distribution with log-normal fitting of the micrograph of Fig. 2(a), (c) selected area diffraction (SAD) pattern, (d) HRTEM lattice fringes of Y15 sample.