Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Cation distribution and magnetic properties of nano and bulk $CoCrFeO_4$ ferrite synthesized by glycine-nitrate combustion method

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ARTICLE INFO

Keywords:
Combustion method
Rietveld refinements
TEM
Magnetic properties

ABSTRACT

Cost effective and low temperature glycine-nitrate combustion method was used to prepare chromium incorporated nanocrystalline and bulk cobalt ferrite $CoCrFeO_4$. The structural properties and phase identification of the samples were studied using X-ray powder diffraction and the Rietveld analysis. Rietveld refinements revealed that both the samples possess cubic symmetry corresponding to the space group $Fd\bar{3}m$. The refinement results also confirm that the cationic distribution over the tetrahedral and octahedral sites in the spinel lattice of both nano and bulk samples is partially inverse. Cr ions invariably occupy the octahedral (*B*) site while Co and Fe ions are distributed over both *A* and *B* sites. The results of *M-H* hysteresis curves revealed that the value of saturation magnetization (M_S) of nanosample is smaller than that of bulk sample. A much larger value of coercivity (H_C) of nanosample (3616G) compared to that of bulk (64G) indicating that they are hard and soft magnets respectively. Magnetization measurements exhibit non-collinear ferrimagnetic structure for the samples.

1. Introduction

Owing to the extremely small dimensions of nanostructured materials, a major portion of the atoms lie at the grain boundaries, which in turn is responsible for superior magnetic, dielectric and mechanical properties in these materials compared to their conventional coarse grained counterparts [1–3]. Recently nanosized ferrite materials have received vital attention due to their potential applications such as electronics, optical devices, ferrofluids, hyperthermia for cancer treatment, coolants, multi layer chip inductors, quantitative immunoassay, drug delivery and gas sensors [4,5]. Spinel ferrites have the general molecular formula AB_2O_4 where *A* and *B* are the divalent and trivalent cations occupying tetrahedral and octahedral interstitial positions of the *fcc* lattice formed by O^{2-} ions. The magnetic properties of these oxides depend on the type of cations and their distribution among the two interstitial positions. The cation distribution and the resulting magnetic properties are found to be different and quite interesting in some nanocrystalline spinel ferrites when compared to those of their bulk counterparts.

The spinel ferrites have remarkable magnetic and electrical properties. Among them, $CoFe_2O_4$ is interesting because of its perfect chemical properties, thermal stability, high electrical resistivity, and excellent magnetic properties [6]. Nanocrystalline $CoFe_2O_4$ with such properties have potential applications in high frequency devices, memory cores, recording media, and in biomedical field [7]. Substitution of other metals for Fe in $CoFe_2O_4$ has been proposed as a method to tailor the magnetic and magneto-elastic properties for sensor applications [8]. Chromium ions (Cr^{3+}) with anti-ferromagnetic nature are known for achieving good control over magnetic parameters in developing technologically important materials. A few previous investigations regarding chromium substituted cobalt ferrites have been reported [9–13]. It is known that the properties of the ferrites depend strongly on their composition and microstructure which are sensitive to the processing methods used to synthesize them. Several methods have been reported to synthesize chromium substituted cobalt ferrite nanomaterials; these include Powder Ceramic technique [11], Micro-emulsion method [12], Chemical Co-precipitation method [13] and Soft citrate gel method [14]. Among these soft-chemical methods, particularly, the combustion synthesis exhibits many advantages and has been used for the large scale production of nanoparticles with high surface area. This method of synthesis is advantageous due to its simplicity, short amount of time and lower consumption of energy during synthesis [15–17]. To the best of our knowledge, there is no report on nanosized chromium substituted cobalt ferrite synthesized by combustion methods. Moreover, there is hardly any report on comparison of this nanosized compound with its bulk counterpart. In view of

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http://dx.doi.org/10.1016/j.ceramint.2017.05.154
Received 30 December 2016; Received in revised form 8 May 2017; Accepted 22 May 2017
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this, we have synthesized bulk and nanosized chromium substituted cobalt ferrite $CoCrFeO_4$ by Glycine-nitrate combustion method and their magnetic properties as a function of both temperature and magnetic field have been investigated.

2. Experimental

$CoCrFeO_4$ was synthesized by Glycine-nitrate combustion method. Combustion reaction synthesis involves a mixture of metal nitrates as oxidizing reagents and a fuel as the reducing agent. For this redox mixture, analytical grade cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$], ferric nitrate [$Fe(NO_3)_3{\cdot}9H_2O$], chromium nitrate [$Cr(NO_3)_3{\cdot}9H_2O$] and glycine (NH_2CH_2COOH) were used for the combustion reaction. Stoichiometric amounts of metal nitrates and glycine were calculated based on the components' total oxidizing and reducing valences, which serve as the numerical coefficients for the stoichiometric balance, so that the equivalence ratio i.e. Φ_e(O/F) is unity and the energy released is maximum [18]. Carbon, hydrogen, chromium, iron, and cobalt were considered reducing elements with respective valences of +4, +1, +3, +3, and +2, while oxygen and nitrogen were considered an oxidizing agents with a valence of −2 and 0 respectively. The total valency of $Co(NO_3)_2$, $Fe(NO_3)_3$ and $Cr(NO_3)_3$, therefore, becomes −10, −15 and −15 respectively which should be balanced by the reducing valency of fuel glycine (equal to 9). Thus, the stoichiometric composition of redox mixture requires −40 + Fm= 0, where F stands for total valency of fuel and m is the number of moles of fuel in order to release the maximum energy. Hence, stoichiometric composition of redox mixture requires 4.44 mol of glycine. Thus, in order to prepare $CoCrFeO_4$, the reactants should be combined in molar proportion of 1:1:1:4.44 of $Co(NO_3)_2$, $Fe(NO_3)_3$, $Cr(NO_3)_3$ and glycine respectively. Based on the above calculations, stoichiometric amounts of reactants were taken and mixed together in an agate mortar and pestle. The slurry was formed as the metal nitrates are hygroscopic in nature. In the combustion process, firstly the slurry was dehydrated at 80 °C which was further heated at 150 °C yielding a voluminous and fluffy product in the beaker. The fluffy powder was heated at 500 °C for 2 h and the resulting product was named as nano. A bulk sample was also prepared by heating a portion of nanosample at 1100 °C for 36 h with a number of grindings and pelletizings. An important advantage of this method is that it does not require water for the preparation of precursor solution and therefore, avoids impurities caused by water completely. According to the principle of propellant chemistry, in the products, primarily the H_2O, CO_2 and N_2 are evolved as gases, when the precursors were used in stoichiometric amounts [18]. Therefore, the combustion reaction for the synthesis of $CoCrFeO_4$ nanoparticles using fuel as glycine can be written as follows,

$$Co(NO_3)_2 6H_2O + Cr(NO_3)_3{\cdot}9H_2O + Fe(NO_3)_3{\cdot}9H_2O + 4.44CH_2NH_2COOH \rightarrow CoCrFeO_4 + 35.11H_2O + 8.88CO_2 + 6.22N_2$$

The structure and purity of the samples were checked at room temperature by means of X-ray powder diffraction (XRD) using CuK_α radiation (λ = 1.5406 Å). The data collection was performed in a 2θ range between 10 and 100° with step-size of 0.017° and step time of 21 s. The surface morphology and microstructures of the samples were studied by scanning electron microscopy FE-SEM Quanta 200 FEG. The elemental analysis of the samples was done by energy dispersive X-ray analysis (EDX) using INCA attachment with the SEM instrument. Transmission electron microscopy (TEM) observation of the samples was performed on a Technai G2 20 S-TWIN FEI Netherlands. The M-H curve at 300 K was measured using Vibrating Sample Magnetometer (VSM, Lakeshore, Model:7410 series). Zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements were performed in the temperature range 80–300 K at 0.1 T magnetic field.

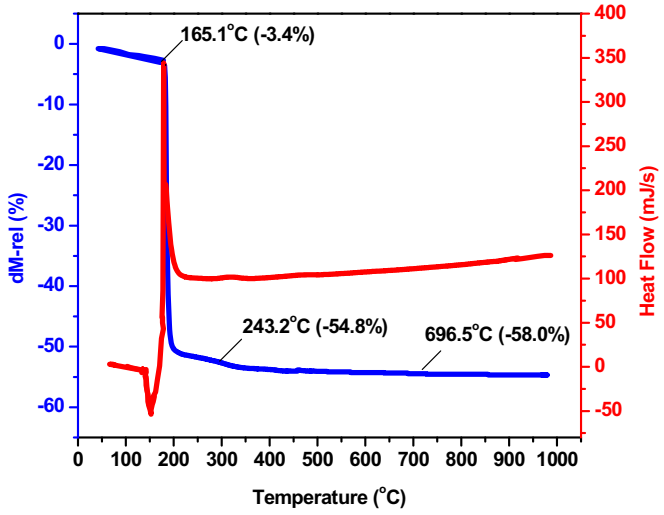

Fig. 1. Thermogravimetric (TG) analysis and differential thermal analysis (DTA) curves for $CoCrFeO_4$.

3. Results and discussion

3.1. Thermo gravimetric analysis (TGA)

Fig. 1 shows the typical TGA curve for as synthesized powder of $CoCrFeO_4$ sample. This figure manifests that the precursor underwent three-step decomposition with increasing temperature from ambient till 1000 °C. In the temperature range 100–200 °C, 4% of weight loss is observed, which is accompanied by an endothermic peak around 200 °C in the DTA Curve. This event is attributed due to the volatilization of the organic solvent and water of crystallization from the wet chemically synthesized ferrite. The second weight loss step occurs in the temperature range of 220–230 °C corresponding to the exothermic peak at around 230 °C in the DTA curve. The weight loss associated with the exothermic reaction is approximately 51%. This is probably attributed to the occurrence of combustion reaction due to the interaction of glycine and nitrate ions in the gel with the liberation of water, CO_2 and N_2 and formation of ferrite, since nitrate ions provided an in situ oxidizing environment for the combustion of organic components [19]. For temperatures from 230 to 900 °C there is approximately 4% weight loss, which shows the stable phase formation of the cobalt chromium ferrite particles above 230 °C.

3.2. Structural characterization

The X-ray diffraction analysis of sintered powders has confirmed the formation of single-phase cubic spinel structure belonging to the space group $Fd\bar{3}m$ without any impurity peak. The broad peaks in the XRD pattern of nanosample indicate a fine particle nature of the powders. After calcination at 1100 °C for 36 h, the reflection peaks of the sample become sharper and narrower, indicating the improvement of crystallinity. Fig. 2 clearly shows that the positions of the reflection peaks for nanopowder are almost identical to the corresponding peaks for the bulk material. This implies that the basic structure of the nanosample is essentially same as that of the bulk material. The structural and compositional details of the phases in both the samples were extracted by the Rietveld refinement of the respective XRD data. The Rietveld refinement was performed using the program GSAS-EXPGUI [20] software packages in the space group $Fd\bar{3}m$. A sixth-order Chebychev polynomial for the background, zero, LP factor, scale, pseudo-Voigt profile function (*U*, *V*, *W* and *X*), lattice parameters and atomic coordinates were used in the refinement. The quality of fit to the observed XRD patterns were assessed by the Rietveld agreement (reliability) factors: *R*-pattern factor (R_p), *R*-weighted pattern factor

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