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Temperature dependent structural and magnetic properties of Cerium substituted Co–Cr ferrite prepared by auto-combustion method

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ABSTRACT

The effects of heat treatment on a nano-crystalline spinel ferrite with chemical formula $CoCr_{0.04}Ce_xF_{e1.96-x}O_4$ (x=0.06) were investigated in the present work. The sample was prepared by the auto-combustion method and then heat treated at 700–1200 °C for 8 h. The sample heat treated at these temperatures was investigated using thermo-gravimetric analyses and differential scanning calorimetry, X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and vibrating sample magnetometery. The XRD patterns and IR spectra confirmed that the synthesized materials were of single phase at and above 900 °C. The average particle size was found to be in the range of 30.8–63.8 nm estimated by the Scherer formula. IR studies confirm two main absorption bands in the frequency range of 400–800 cm^{-1} arising due to the tetrahedral (A-site) and octahedral (B-site) stretching vibrations. The average grain size increased with the increase of temperature while distribution of particles became homogeneous as observed by scanning electron microscope. The saturation magnetization was increased gradually from 7.4 to 59.6 emu/g with the increase of temperature. The coercivity lies in the range of 248–811 Oe as a function of temperature. The obtained results suggest that the investigated materials may be potential candidates for high density recording media applications.

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1. Introduction

Nanomaterials have attracted numerous scientists all over the world due to their versatile and many applications. Nanostructured spinel ferrites have been widely used in microwave absorption materials, microwave devices (isolators, circulators, phase shifters), magnetic drug delivery and high density storage media, fabrication of radio frequency coils, transformer core, and telecommunication devices [1]. Cobalt based ferrites are important due to their magnetic properties, high electrical resistivity, high saturation magnetization and low eddy current losses [2]. It is interesting that, the desired structural and magnetic properties of the soft ferrites for a particular application can be tailored by varying the type and amount of substituent into the spinel lattice. Many groups have reported the behavior of ferrites by substituting trivalent ions (Cr^{3+},Al^{3+}) in place of iron Fe^{3+} including rare earths ions [3,4] like cerium, due to its variable electronic structure and its application in making a permanent magnets. In this connection, the effects of rare earth substitution on the properties of spinel ferrites have been reported by many researchers [5–9]. Also magnetization in spinel ferrites is due to the interaction between A and B-sites. *M–H* square loop with remanance ratio 0.5 is the prime requirement in recording and memory cores [10]. Furthermore, the cations in the spinel structure play an important role in determining the magnetocrystalline anisotropy in the 4f–3d inter-metallic compounds. It is known that the magnetic behavior of the ferromagnetic oxides is largely governed by the Fe–Fe interaction (the spin coupling of the 3d electrons). By introducing rare earth R-ons into the spinel lattice, the R–Fe interactions also appear (3d–4f coupling), which can lead to small changes in the magnetization and Curie temperature of these ferrites. The R–R interactions are very weak since they result from the indirect 4f–5d–5d–4f mechanism [11,12]. Huang and Guoa et al. [13–15] have studied the properties of one-dimensional (1D) and quasi-one-dimensional (Q1D) ceramic nanostructures such as fibers, wires, rods, belts, tubes, spirals, and rings. These types of materials have attracted a great interest owing to their potential applications in

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many technologically important areas such as gas sensing, electronics semiconductor, electrical characteristics, photonics (photocatalysis) and magnetic applications. Huang et al. [14] have also synthesized the $Co_xZn_{(1-x)}Fe_2O_4$ ferrite nanofibers by the electrospinning method. Lightweight properties with a low surface density of 2.4 g/m^2 have been described. It was reported that these materials exhibit excellent microwave absorption having a reflection loss −10 dB in the X-band and 80% of the Ka-band frequency. Recently, several methods have been employed to synthesize highly crystalline nano-particles of spinel ferrite and the most common methods are co-precipitation [16], hydrothermal [17], combustion [18], microemulsion [19], polymer-pyrolysis [20], sol–gel [21], etc. The auto-combustion method has gained importance during the last few decades. This process offers many advantages as compared to the conventional powder route, such as low temperature processing and/or better homogeneity for the synthesis of multi-component materials and thus formation of the nano-sized particles of ferrites. The main focus of this work was to investigate the effects of heat treatment on the structural and magnetic properties of cerium substituted $CoCr_{0.04}Ce_{0.06}Fe_{1.90}O_4$ ferrites that were prepared by auto-combustion method.

2. Experimental methods

The chemical regents including $CO(NO_3)_2 \cdot 6H_2O$ (Aldrich, 98%), $Cr(NO_3)_3 \cdot 6H_2O$ (Aldrich, 98%), $Fe(NO_3)_3 \cdot 9H_2O$ (Aldrich, 99%), $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich, 98%), monohydrate citric acid $C_6H_8O_7 \cdot H_2O$ (Fisher, 99.91%) and ethanol were used to prepare the samples having the general formula $CoCr_{0.04}Ce_xFe_{1.96-x}O_4$ ($x=0.06$). The auto-combustion method was employed to prepare the ferrite material. The stoichiometric amounts of high purity metal nitrates and citric acid were dissolved into de-ionized water to form a mixed solution. Homogenous distribution and segregation of the metal ions were achieved by the use of citric acid. The ammonia solution (30%) was added drop wise to maintain pH value at about 7–8. The resulting solution was constantly heated at 80 °C and stirred on a magnetic stirrer with hot plate. A gel of citrate precursors was formed after 5 h of continuous stirring and heating. An increase in the temperature up to 200 °C led to the ignition of dry gel and a loose ferrite powder was obtained through the burning of gel in a self-propagating combustion manner. During the combustion process, exothermic decomposition of the redox mixture of metal nitrates and citric acid took place along with the removal of gases such as chlorine, carbon monoxide and carbon dioxide. The prepared dried powder was then put in alumina crucible and subsequently heat treated for 8 h in a temperature range of 700–1200 °C with an interval of 100 °C. Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) were employed to analyze the thermal behaviors of the as-obtained powder. The measurements were taken on a Netzsch Sta 409 instrument, with Al_2O_3 as the inert reference material, from room temperature to 1200 °C, at the rate of 10 °C min^{-1}. The Fourier transform infrared spectra (FT-IR) were measured in the range 400–4000 cm^{-1} using Jasco-310 spectrometer. The X-ray diffraction (XRD) patterns were obtained at room temperature using powder samples in an Xpert Pro PANalytical diffractometer with Cu-Kα radiation ($\lambda = 1.54056$ Å) at 40 kV and 30 mA. Intensity data were collected by the step counting method (with a scanning speed 0.05°/s) in the 2θ range from 15°–70°. The surface morphology and microstructure of the samples were studied by JSM-6490 JEOL scanning electron microscope (SEM), equipped with energy dispersive (EDX) unit model JFC-1500 JEOL. The Magnetic measurements were carried out at room temperature using vibrating sample magnetometer (Lake Shore 7404) with a maximum applied magnetic field of 15 kOe.

2.1. Calculations

The structural parameters like lattice constant 'a', unit cell volume, X-ray density, crystallite size 'D' and lattice strain B_G^2 were calculated from XRD data using the formulae described earlier [21–24].

$$D = \frac{k\lambda}{B_{(hkl)}\cos\theta} \tag{1}$$

$$B_G^2 = 8\pi(\tan^2\theta)(\varepsilon_{rms}^2) \tag{2}$$

Eqs. ((1) and 2) were used to calculate the crystallite size (D) nm and root mean square lattice strain ϵ_{rms}, respectively. Here k is the shape factor, λ is the X-ray wavelength and θ is the Bragg's diffraction angle and B_G is the integral width (defined as the peak area divided by peak height) of peak in radian.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) plots of the prepared material that were performed up to temperature of 1200 °C at the heating rate of 10 °C min^{-1} in argon gas to observe different changes and transformation of different phases during the heat treatment. The DSC plot shows three endothermic peaks centered at 395 °C, 440 °C and 510.7 °C. The endothermic peak that appeared at a temperature of about 510.7 °C may be assigned to the formation of mixed ferrite as well as the beginning of the formation of the spinel phase. In the literature some studies are available showing that the presence of free excess citric acid (chelating agent) and nitrate complications the decomposition processes. The decomposition is very complex and proceeds through three to four major processes, which include the removal of water and excess nitrates, decomposition of anhydrous citrate complex carbonates leading to spinel ferrite formation. However, the excess citric acid helps in reducing the particle size as a large number of gases, i.e. CO, CO_2, organic products (acetone dicarboxylate) water vapor, etc., evolve during the decomposition process that help in inhibiting the particle size growth [25]. TGA curve shows that above the temperature 600 °C the behavior of the curve becomes linear. The

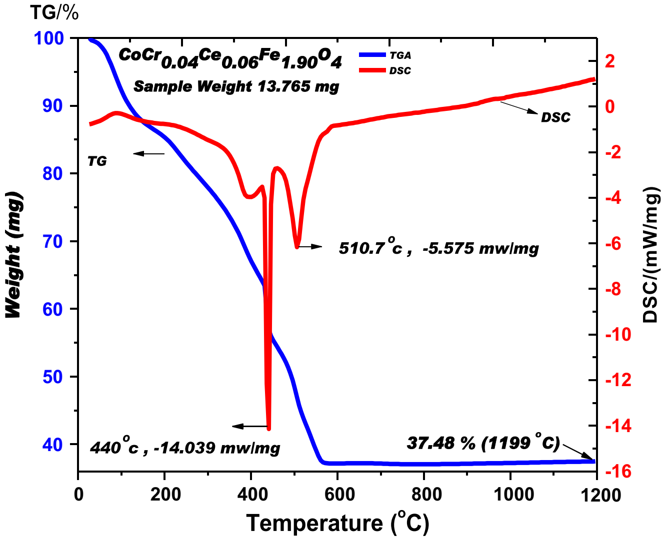

Fig. 1. TGA and DSC profiles of the as-prepared powder sample $CoCr_{0.04}Ce_{0.06}Fe_{1.90}O_4$.

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