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Research articles

Zr doping dependence of structural and magnetic properties of cobalt ferrite synthesized by sol–gel based Pechini method

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ABSTRACT

Nanocrystalline $CoZr_xFe_{2-x}O_4$ ($0 \leq x \leq 0.3$ in a step of 0.05) powders were synthesized by Pechini sol–gel method. The dry gel was grinded and calcined at 700 °C in a static air atmosphere for 1 h. Some tests such as thermo gravimetric analysis (TGA) combined with differential analysis (DTA), fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and vibrating sample magnetometer (VSM) were carried out to investigate the thermal behaviour, structural bonds identification, crystallographic properties, morphology and magnetic properties of the obtained powders. X-ray diffraction revealed a single-phase cubic spinel structure for all samples, where the crystallite size decreases; the lattice parameter simultaneously increases with substitution of Zr. The results of FE-SEM showed that the particle size is in the 20–70 nm range. The magnetic properties such as saturation magnetization (*Ms*), remanent magnetization (*Mr*) and coercivity (*Hc*) were measured from the hysteresis loops. The greatest amount of saturation magnetization for $CoZr_{0.05}Fe_{1.95}O_4$ sample was 67.9 emu·g^{-1}.

1. Introduction

In recent years, the interest in investigating of nano-size materials has increased due to their unusual physical and chemical properties which are often different from the bulk counterpart [1,2]. Ferrites are ferrimagnetic oxides and therefore are electrically insulating, widely used in high-frequency applications, because an AC field does not induce undesirable Eddy currents in an insulating material [3,4].

Cobalt ferrite ($CoFe_2O_4$) magnetic nanoparticles which have moderated magnetization have long been known for its versatile applications including information storage, ferro fluid technology, medical diagnostics, magnetic refrigeration, and magneto mechanical devices [5–7]. The use of cobalt ferrite in various applications requires its various magnetic properties. The several numbers of modifications have been carried out to enhance its characteristics both magnetically and electrically to make a potential material for wide range of applications such as magnetic recording and storage, spin filters, spintronics and phase shifters [6].

The structural formula for a generic spinel compound MFe_2O_4 (M = Co, Mn, Ni, Zn, Mg, etc.) can be written as [8,9]:

$$(M_{1-i}Fe_i)^A[M_iFe_{(}(2-i))]^BO_4$$

where the amounts in brackets represent the average occupancy of A (tetrahedral sites) sites and B (octahedral sites) sites and *i* is the inversion parameter. The spinel structure is complex because molecules do not always correspond fully to a normal or an inverse structure. Hence, an inversion parameter, *i*, defined by $0 < i < 1$ is introduced. For $CoFe_2O_4$, *i* range from 0.68 to 0.8 meaning that between 68% and 80% of Co^{2+} ions occupy octahedral sites rather than 100% of Co^{2+} ions occupying octahedral sites, which is the case for a fully inverse spinel structure, described above [9,10].

The magnetic properties of a spinel are sensitive to the types of cation and their distribution amongst the two interstitial sites of spinel lattice [11,12]. Any change in distribution of cations among tetrahedral and octahedral site alters the spin order which strongly affects the magnetic and electric properties of cobalt ferrite. The incorporation of dopant at any preferable site not only brings change in magnetic moment but also controls the particle growth which can bring changes in cation distribution and ultimately controls material behaviours [13–15].

Cobalt ferrite nanoparticles presents suitable physical, chemical and magnetic properties like high coercivity (5400 Oe) [16], high chemical stability, high Curie temperature 520 °C [17], high anisotropy constant (2.65×10^6–5.1×10^6 erg·cm^{-3}) [18] and a

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moderate saturation magnetization at room temperature of 80 emu·cm^{-3} [19].

In order to obtain ultrafine particles for use in high density magnetic recording media, it is essential to find the best synthesis conditions [20]. Several kinds of techniques can be used to synthesis of the mixed oxide ceramic powders. Ferrite powders have been reported to be synthesized by various routes, such as mechanical milling [21,22], sol–gel [23,24], co-precipitation [25–27], combustion route [28], etc.

Among the above-mentioned processes, the cobalt ferrite powders have been synthesized using sol–gel based Pechini method and their structural properties have been studied by Fourier transform infrared (FTIR) spectroscopy, powder X-ray diffraction (XRD) studies and field emission scanning electron microscopy (FE-SEM). Vibrating sample magnetometry (VSM) has been used to investigate their magnetic properties.

Recent studies indeed predict new fascinating properties for substituted cobalt ferrite that depends on cation distribution and the electronic state of the transition metal ions of the spinel structure [16]. Since Zr^{4+} is known to have strong preference for tetrahedral coordination [29–33], the aim of the present investigation, therefore, is to study the substitution of Zr^{4+} for Fe^{3+} in the Co ferrite lattice and its subsequent effect on the structural and magnetic properties of cobalt ferrite.

2. Experimental

2.1. Materials synthesis

Nanocrystalline Co ferrite spinels were synthesized by sol–gel based Pechini process. All chemicals used in this study were of analytical grade and used without any further purification. The sol–gel synthesis was based on the formation of a stable and homogenous solution. The chemical reagents for this experiment are Stoichiometric amounts of Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), Zirconium (II) nitrate hydrate ($ZrO(NO_3)_2{\cdot}xH_2O$), Iron (III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$), Citric acid ($C_6H_8O_7{\cdot}H_2O$) and Ethylene glycol ($C_2H_6O_2$). For all the samples preparation, the metal nitrates were dissolved together in distilled water using a magnetic stirrer, which is a hydrolysis reaction. At 60 °C, Citric acid was added to solution. Then Ethylene glycol was added to solution at 80 °C. After that the solution was then heated at 80–90 °C until a wet gel of the metal nitrates was obtained. The wet gel was then dried at 185 °C for 24 h in oven. Finally, the dry gel was grinded and calcined at 700 °C in a static air atmosphere for 1 h.

2.2. Instrumental details

The samples were characterized by the X-ray diffraction using Burker/D8 diffractometer ($Cu_{K\alpha}$ radiation λ = 1.5418 Å) and differential thermal analysis and thermo gravimetric analysis (DTA/TGA) using a 409 PC-Netzsch instrument with a heating rate of 5 °C·min^{-1} in the air atmosphere. Field emission scanning electron microscope (FE-SEM; Model Mira3-XMU, TESCAN) equipped with energy dispersive X-ray spectroscopy was employed to characterize the morphologies and particle size of the nanocrystals. Energy dispersive X-ray micro-analyzer was used to probe the constitutive elements into the samples. The magnetic properties of the all samples were investigated by vibrating sample magnetometer (VSM; Model Kavir magnet) with a maximum applied field of 10 kOe at room temperature.

3. Results and discussions

3.1. Phase identification and crystallite size

Fig. 1a shows the X-ray diffraction pattern of the calcinated $CoZr_xFe_{2-x}O_4$ ($0 \le x \le 0.3$ in a step of 0.05) samples. The peaks were followed and observed in all the samples and successfully indexed as (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes of cubic spinel phase of $CoFe_2O_4$ [34]. All peak positions were used in the determination of precise lattice parameters. Structural refinements were carried out using the Rietveld program Maud [35]. Peak profiles were fitted with a pseudo-Voigt function and an asymmetry parameter was considered for peaks below 90° 2θ. It was observed that all XRD peaks could be indexed to $CoFe_2O_4$ with Fd3m space group. Also physical and theoretical properties of produced ferrite through mathematical equations using XRD results were calculated. The calcined nanocrystal crystallite size was calculated by the formula 1 (Scherrer's relationship) [36]:

$$D = \frac{k\lambda}{\beta Cos\theta} \quad (1)$$

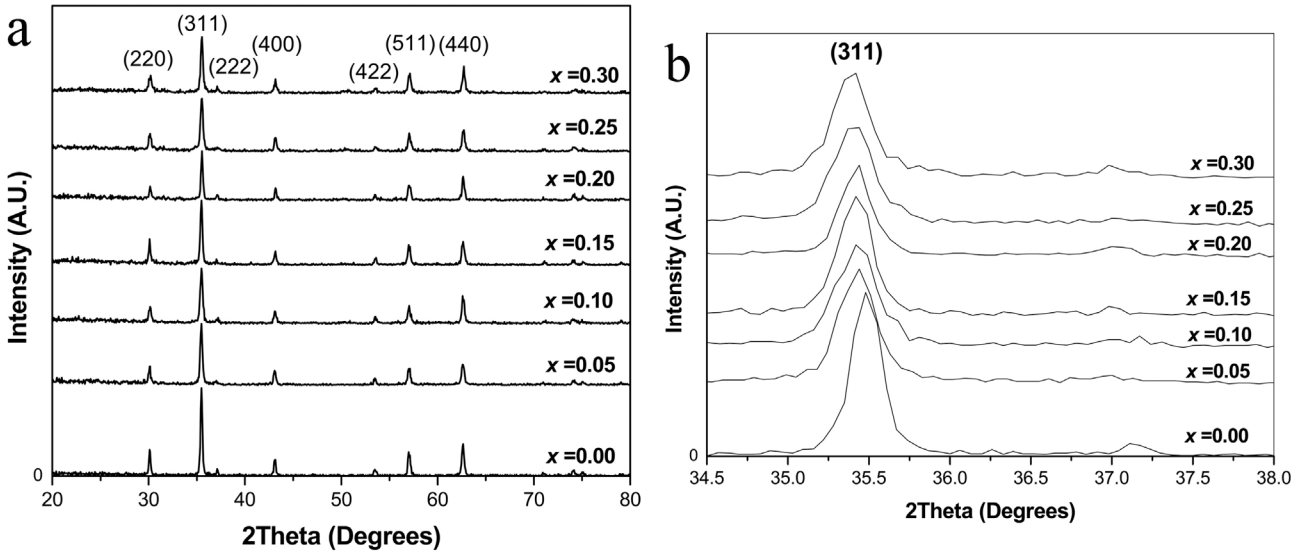

Fig. 1. X-ray diffraction pattern (a) of calcined $CoZr_xFe_{2-x}O_4$ ($0 \le x \le 0.3$) samples and (b) peak position of (3 1 1) peak.