Middle East Journal of Applied Sciences
ISSN 2077-4613

Volume : 06 | Issue :02 |April-June| 2016
Pages: 362-366

Characterization of Sol-gel Fabricated Cobalt Ferrite $CoFe_2O_4$ Nanoparticles

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Received: 10 April 2016 / Accepted: 15 May 2016 / Publication date: 30 May 2016

ABSTRACT

Spinal $CoFe_2O_4$ nanoparticles catalyst is synthesized by a simple sol gel process through the hydrolysis and condensations at a temperature lower than 500ºC. The structure and magnetic characterization of the produced nanoparticles are achieved using X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and VSM.The X-ray diffraction pattern confirmed high crystalline degree and cubic structure of $CoFe_2O_4$ calcined at 400ºC for 4h in air. The FT-IR spectra reveal the stretching vibration of octahedral complexes of Fe–O through the observed band around 595 cm^{-1}. Ferrimagnetic hysteresis loop and saturation magnetization of 36 emu g^{-1} was elucidated by VSM.

Key words: Ferrite nano-materials, Sol gel (Xerogel), Ceramics; Nanocrystals.

Introduction

Nanostructure ferrites (MFe_2O_4) materials have been found in a broad range of applications in many areas such as magnetic fluids for retrieval and storage of information, magnetic recording media, magnetic resonance imaging enhancement, magnetically guided drug delivery, catalysis, sensors, pigments etc. (Vasundhara *et al*., 2013; Sangmanee and Maensiri, 2009). So, it gained high interest in last decades because of their excellent magnetic and electrical properties (Vasundhara *et al*., 2013; Sangmanee and Maensiri, 2009; Trad *et al*., 2011; Zhang *et al*., 2006). Spinel ferrite has a general chemical formula MFe_2O_4 where M is the divalent metal ion such as Mn, Zn, Ni …etc.

Cobalt ferrite $CoFe_2O_4$ nanoparticle is one of the most fascinating ferrites (MFe_2O_4) that attract a lot of attention because of its remarkable magnetic properties, relatively large magnetic anisotropy and moderate saturation magnetization. Cobalt ferrite ($CoFe_2O_4$) belongs to inverse spinel structure in which half of Fe^{3+} ions occupy tetrahedral sites and the other half occupy the octahedral sites with Co^{2+} ions. In the inverse spinel structure the magnetic moment of Fe^{3+} in the tetrahedral sites is aligned in opposite direction to that of Fe^{3+} in the octahedral sites and hence the net magnetic moment produced from Fe^{3+} is zero. So the net magnetic moment of $CoFe_2O_4$ is due to the magnetic moment of Co^{2+} in the octahedral sites (Zhang *et al*., 2005).

The distribution of unpaired magnetic moment of Co^{2+} in the octahedral sites results in magnetocrystalline anisotropy in $CoFe_2O_4$, so cobalt ferrite belongs to ferromagnetic materials. $CoFe_2O_4$ with three-dimensionally framework structure linked FeO_4-tetrahedra and good magnetic properties make this ferrite an excellent core material for power transformers in electronics, memory and telecommunication applications (Goldman, 2005; Kahlenberg and Fischer, 2001).

Sol–gel technique has been developed to produce magnetic and electrical materials. So, the sol–gel process considers an attractive chemical method for the formation of high purity, high homogeneity and porous structures, ceramics and films at low temperature (Brinker *et al*., 1992; Elnahrawy and Ali, 2014)[8, 9]. Moreover, the sol–gel materials provide the possibility of controlling the shape, size and distribution of the particles in the system (Yang *et al*., 2009; Haroun *et al*., 2014; Elabd *et al*., 2016).

This work concern to prepare cobalt ferrite ($CoFe_2O_4$) using the sol gel method using aqueous solutions of ferric nitrate, cobalt nitrate, citric acid and ethylene glycol at lower calcinations temperature to improve the structural and magnetic properties. The structural and magnetic behavior of $CoFe_2O_4$ nanoparticles has been studied.

Experimental

Materials

All the chemicals used for synthesis were of analytical grade. Cobalt nitrate ($Co(NO_3)_2$ -$6H_2O$), ferric nitrate($Fe(NO_3)_3$ -$9H_2O$), citric acid ($C_6H_8O_7.H_2O$), ethylene glycol, and all chemicals were used without any further purifications.

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Synthesis of cobalt ferrite ($CoFe_2O_4$) nanoparticles

$CoFe_2O_4$ nanoparticles were prepared by sol–gel method through hydrolysis and condensation. Cobalt ferrite nano-particle was prepared with the following steps:(i) The nitrates of (Fe^{3+}:Co^{2+}ions, 2:1 molar ratio) were dissolved individually in ethylene glycol under magnetic stirring for 30 min. (ii) Added a certain amount of citric acid to the previous solutions (iii) added both solutions to each other and stirred at 80°C until a clear and viscous sol was obtained (iv) the viscous sol was dried at150°C for 10h; and (iiv) the dried gel was calcined at 400°C for 4h in air. The prepared $CoFe_2O_4$ nanoparticles were characterized by X-ray diffraction (XRD) and Fourier transform inferred (FTIR). The average crystallite size was calculated from the most intense peak (311) by using the Scherrer's formula (Berry and Curtis, 2003).

$$G = \frac{k\,\lambda}{D\ cos(\theta)}$$

where k = 0.9 is the Scherrer constant, λ = 1.54056Å is the wavelength of X-ray, and D is the full width at half maximum intensity (FWHM) of the peak. The magnetic analysis for the prepared nanoparticles was determined using vibrating sample magnetometer (VSM).

Results and Discussions

Structural analysis-XRD

Fig. 1 represents the indexed XRD pattern of the prepared cobalt ferrite $CoFe_2O_4$ nanoparticles. The broadening of the diffraction peaks confirms the formation of nanostructure $CoFe_2O_4$. As seen from the Fig. the XRD shows a good poly crystalline $CoFe_2O_4$. All peaks of the prepared sample and its position at 2θ scale are completely compatible with the characteristic peaks of cubic spinel $CoFe_2O_4$ and they are matched with the XRD card no.22-1086. As seen from Fig.1 there is no other peakes related to cobalt oxide, iron oxide or other phases which indicate that we have pure cubic spinel $CoFe_2O_4$.

The crystallite size for $CoFe_2O_4$ was found to be 30nm.

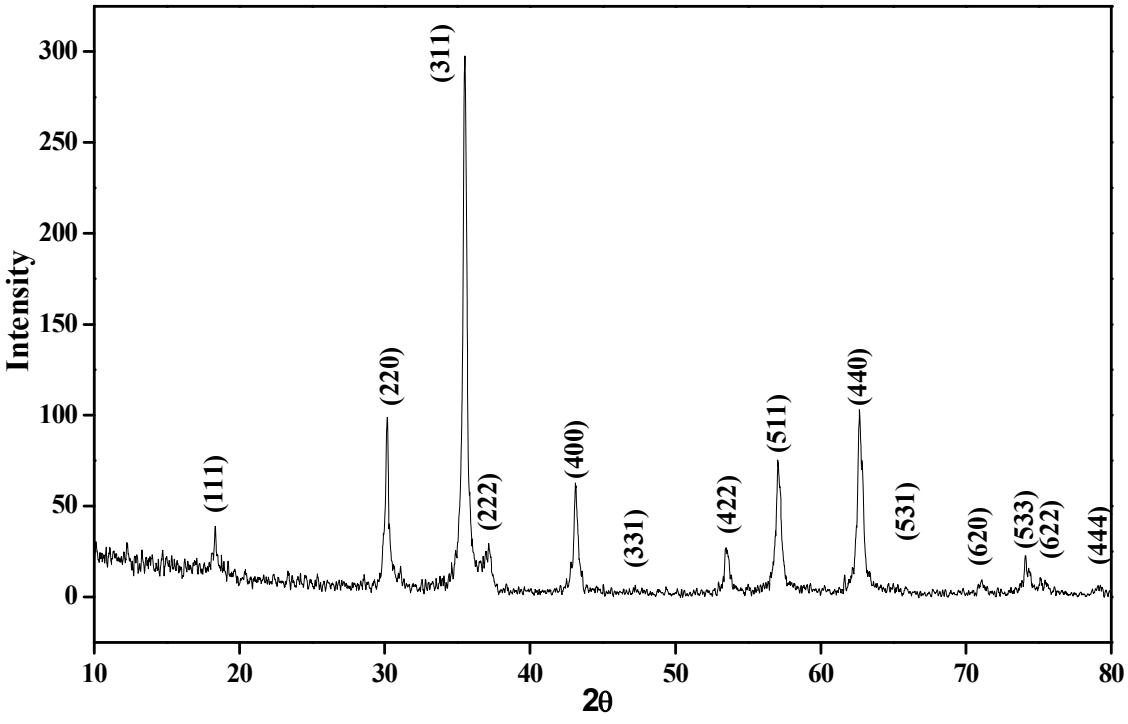

Fig. 1: X-ray diffraction (XRD) pattern of the prepared $CoFe_2O_4$ nanoparticles.

FTIR analysis

Since cobalt ferrite ($CoFe_2O_4$) has a spinel structure, so it characterized by octahedral and tetrahedral site. FTIR spectra give good information about the distribution of cations between octahedral and tetrahedral sites in the spinal ferrite. Fig. 2 shows that the FTIR spectrum of $CoFe_2O_4$ has two distinct absorption bands around 426 and 582 cm^{-1}. The absorption band around 426 cm^{-1} distinguishes the stretching vibration frequency of the metal-oxygen at the octahedral site from the stretching vibration of the metal-oxygen at the tetrahedral site which has absorption band around 582 cm^{-1}. These two metal-oxygen vibrational bands are the characteristic bands of $CoFe_2O_4$ (Pui *et al*., 2011; Vasundhara *et al*., 2013; Wu *et al*., 2014). The absorption band at 943 and 1020 cm^{-1} may be assigned to the bending vibration of C-H and stretching vibration of C-N, respectively. 1020 cm^{-1} may be corresponding to the nitrate traces (Sangmanee and Maensiri, 2009) . The band at 1428 cm^{-1} was assigned to symmetric vibration (COO-) of the carboxylate group bonded to the nanoparticle surface. The 1641 cm^{-1} band is due to the deformation mode of absorbed H_2O molecules, assigned to the bending vibration. The absorption band of symmetric and asymmetric vibrations of CH_2 groups appeared at 2926 and 2853 cm^{-1}, respectively, which can be attributed to organic residues (Li *et al*., 2010; Cannas *et al*., 2010). The broad band with a maximum around 3461 cm^{-1} assigned to O–H stretching vibration of the surface adsorbed water from moisture content in the sample (Trad *et al*., 2011).

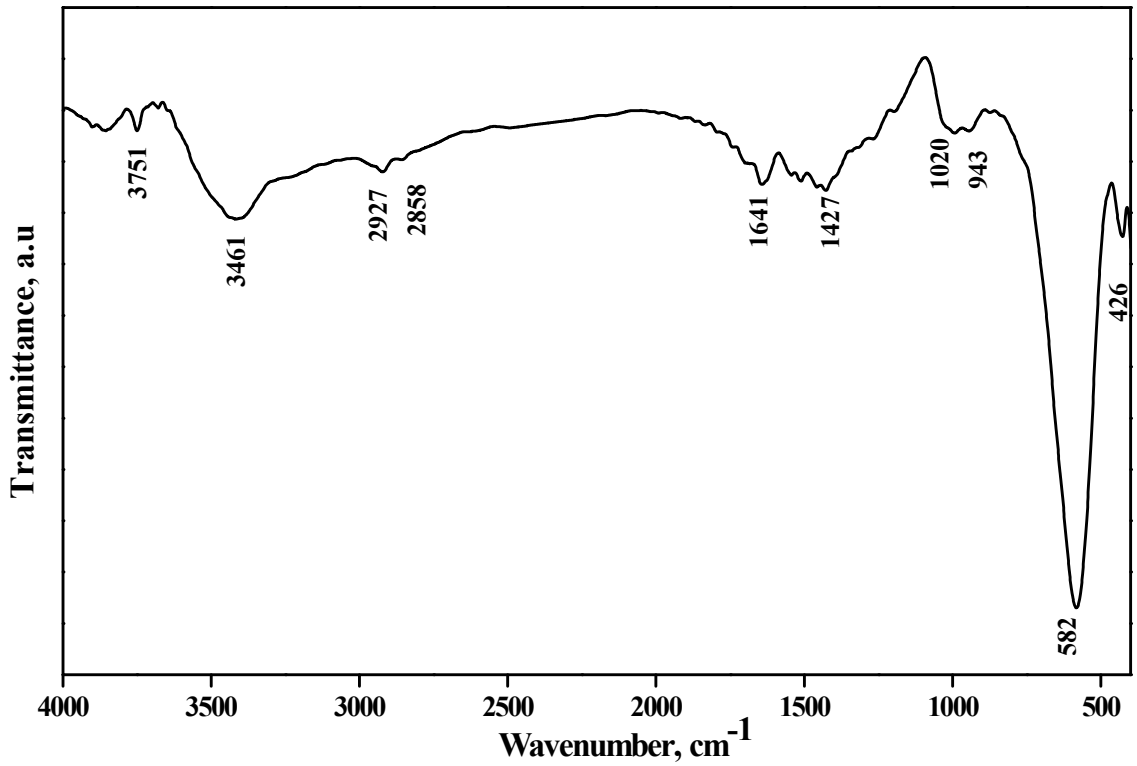

Fig. 2: FTIR spectrum of the prepared $CoFe_2O_4$ nanoparticles.

Magnetic properties

Fig.3 demonstrates that $CoFe_2O_4$ calcined at 400 ^oC for 4h in air has a well saturated magnetic hysteresis loop in the field range ±20KOe, which confirm the presence of magnetic order in the structure of the prepared samples.

The saturation magnetization (M_s) reached to 60.67 emu/g which is less than that of bulk cobalt ferrite (80.8 emu/g), also the prepared nanoparticle has a lower value of remanant magnetization (M_r) (13 emu/g). The lowering values of the saturation magnetization and the remanant magnetization can be attributed to the presence of magnetic disordered at the surface of the nanoparticles, which cover the magnetic ordered at the core of the nanoparticles. This disordered is known as spin glass. The effect of spin glass increases with decreasing the particle size and hence the saturation magnetization (M_S) and the remanant magnetization (M_r) lowered to small values (Kurtan *et al*., 2013; Thang *et al*., 2005; Maaz *et al*., 2007; Kumar *et al*., 2008).

The coercivity and the remanant ratio (M_r/M_s) of $CoFe_2O_4$ were found to have small values 346 Oe and 0.21 respectively. According to Stoner–Wohlfarth model the small value of the remanant ration (M_r/M_s) represents uniaxial anisotropy for noninteracting single domain particles with randomly oriented easy axis.

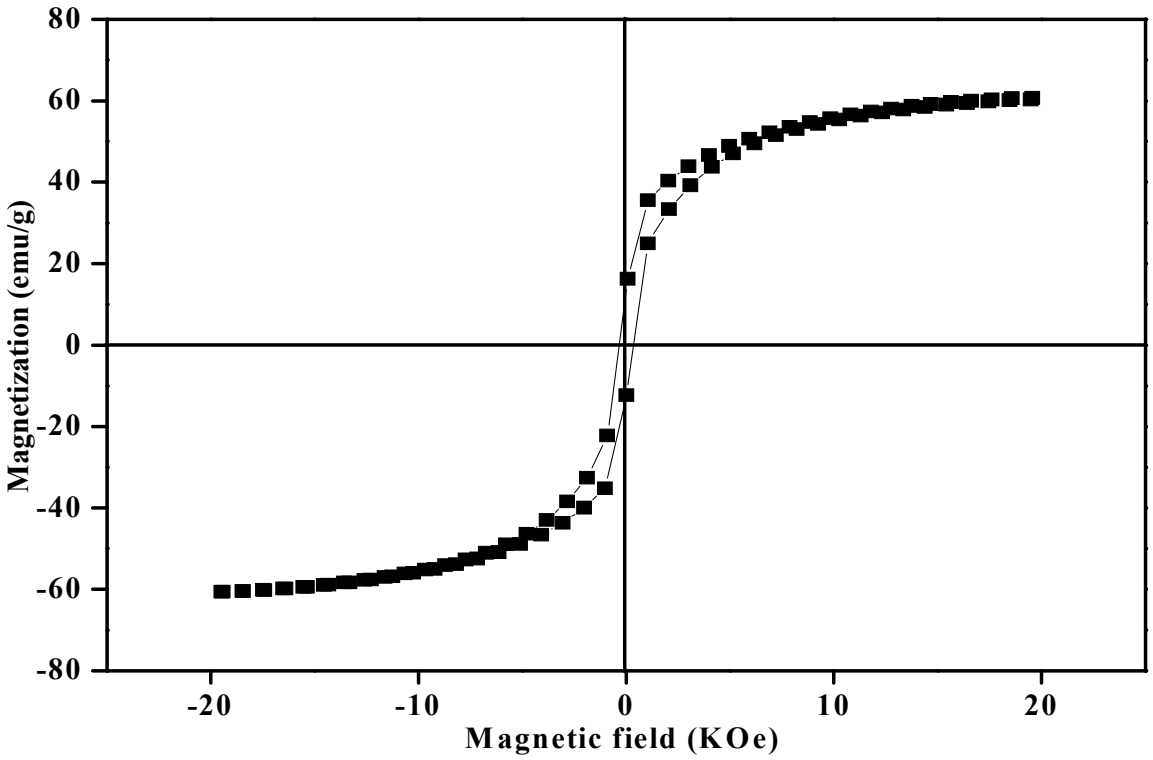

Fig. 3: Hysteresis loop of the prepared $CoFe_2O_4$ nanoparticles.

Conclusions

Low temperature sol–gel process was used to prepare $CoFe_2O_4$ gel from metal nitrate and citric acid. X-ray diffraction assured the cubic phase spinel structure for the investigated sample with crystalline size 30 nm. M-H loop confirm the presence of the ferromagnetic ordered in $CoFe_2O_4$ prepared at lower temperature. These results introduce the sol–gel autocombustion process as a novel synthesis technique having the advantages like low cost, simple preparation and a resulting nano-sized powder.

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