



Characterization of Mg²⁺ substituted Cobalt ferrite nano particles synthesized by sol-gel method

Chemistry

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ABSTRACT

In the present study samples of Mg_xCo_{1-x}Fe₂O₄ (x = 0.0, 0.5, and 1.0) ferrite nanoparticles were synthesized by the sol-gel auto combustion technique and the samples were sintered at 800 °C for 4 h. X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were employed for characterization. XRD studies confirms the formation of single phase spinel structure with crystallite size in the range of 50–69 nm.

KEYWORDS:

Sol-Gel, Nanoferrite, FTIR, XRD, SEM

1. Introduction

Spinel ferrites with the general formula AFe₂O₄ (A = Mn, Co, Ni, Mg, or Zn) are very important magnetic materials because of their interesting magnetic and electrical properties with chemical and thermal stabilities. These properties make them suitable for different applications in information storage system, sensors, catalysis, magnetic drug delivery, permanent magnets, recording heads, antenna rods, loading coils, telecommunication devices, magnetic refrigeration, magnetic recording heads, antenna rods etc.(1-3). Magnesium ferrite (MgFe₂O₄) is one of the most important ferrites. It has a cubic structure of normal spinel-type and is a soft magnetic *n*-type semiconducting material,

On the other side, cobalt ferrite (CoFe₂O₄) has an inverse spinel structure in which, Co²⁺ ions are in B sites, and Fe³⁺ ions are equally distributed between A and B sites. Cobalt ferrite has been widely studied due to its high electromagnetic performance, excellent chemical stability, mechanical hardness, high coercivity, and moderate saturation magnetization, which make it suitable for the electronic components used in computers, recording devices, and magnetic cards (4-6). These properties are dependent on chemical composition and microstructural characteristics, which can be controlled in the fabrication and synthesis process. It has been observed that when cobalt ferrite substituted with cations like Mn, Zn, Ni etc, the properties of cobalt ferrite are modified (7-8). Substitution of non-magnetic magnesium ion with magnetic cobalt ion may modify their magnetic and electrical properties.

Spinel ferrites can be synthesized by various techniques viz., standard Ceramic method, Chemical co-precipitation method, Solid state reaction, Hydrothermal process, Micro-emulsion method and sol-gel method (8-13). In recent years, various methods have been reported for synthesis of pure and substituted cobalt ferrite nanoparticles (14). Among the various methods. Citrate Solgel auto combustion technique has been preferred as this method provides an easy alternative for the synthesis of various nano crystalline ferrites at low temperature sintering itself.

Present investigation is to study the synthesis and structural properties of magnesium substituted cobalt ferrite nano particles by the solgel auto combustion technique.

2. Materials and Methods

2.1. Sample preparation

In this study, samples of nanocrystalline ferrite with the formula Mg_xCo_{1-x}Fe₂O₄ (x=0,0.5 and 1.0) were synthesized by the citrate gel auto combustion method. AR grade chemicals such as cobalt nitrate-Co(NO₃)₂·6H₂O, magnesium nitrate-Mg(NO₃)₂·6H₂O, ferric nitrate-Fe(NO₃)₃·9H₂O and citric acid C₆H₈O₇·H₂O were used for the synthesis. Calculated quantities of metal nitrates were dissolved in double distilled water and required amount of aqueous citric acid solution was added that act as a organic fuel. The molar ratio of metal nitrate to citric acid was adjusted as 1:1. The mixture was placed on a magnetic stirrer for thorough stirring to get a homogeneous solution. Ammonia solution was added to this nitrate-citrate mixture to adjust the pH to

7. The mixed solution was heated on a magnetic hot plate at about 100 °C with uniform stirring and was evaporated to obtain a highly viscous gel as precursor. The resultant gel was further heated on a hot plate until all water molecules were removed from the mixture, the viscous gel began frothing. The gel gave a fast flameless self ignited combustion reaction with the evolution of large amounts of gaseous products. The reaction was completed in a minute giving rise to dark gray product. The synthesized powders were sintered at 800 °C for 4 h in air at a slow heating rate of 5 °C/min and then furnace was cooled to room temperature. The cooled samples were ground using mortar and pestle for getting fine powdered samples.

2.2 Characterization

The phase identification and crystalline structure analysis of all samples were determined by XRD using a X-ray diffractometer (SmartLab) with a CuK α radiation ($\lambda=1.5405\text{\AA}$). Scanning electron microscopy (SEM) (ZIESS EVO18) was used to investigate the morphology of the samples. The Fourier transform infrared spectroscopy (FTIR) of samples of Co-Mg ferrites were recorded on Perkin Elmer spectrometer using KBr pellets.

3. Results and Discussion

3.1. XRD analysis

X-ray diffraction pattern of the prepared samples of ferrite was shown in Fig.1(a)(b)(c). All Bragg's reflections have been indexed as (111), (220), (311), (400), (511), (440), (620) and (533), (723) which confirmed the formation of well-defined single phase cubic spinel structure that belongs to the space group Fd3m with JCPDS card numbers 22-1086 and 89-3084 without any impurity peak. The strongest reflection was observed from the (311) plane that indicates the spinel phase. An average Crystallite size (*t*) was determined from broadening of the respective high intensity (311) peak by using the Debye-Scherrer formula:

$$t = 0.9\lambda / \beta \cos \theta$$

where *t* is the crystallite size (nm), λ is the wavelength of x-ray ($\lambda=1.5405\text{\AA}$), β is the Full Width at Half Maxima (FWHM) in radians and θ is the Bragg's angle at the peak position. The crystallite size varies in between 50.8 and 43.7 nm as a function of magnesium concentration, *x* (Table 1).. The lattice constant (*a*) of Co-Mg nanoparticles was determined using relation;

$$a = d(h^2 + k^2 + l^2)^{1/2}$$

where *a* = lattice constant, *d* = interplanar spacing and *h, k, l* = Miller indices. Values of lattice constant of ferrites are given in Table 1. Lattice constant for cobalt ferrite was obtained 8.387 which is in a good agreement with the reported values. It was observed that in case of Mg_{0.5}Co_{0.5}Fe₂O₄, lattice constant lies in between cobalt and magnesium ferrite.

3.2 FTIR studies

The FTIR spectra were recorded at room temperature in the frequency range 400-4000 cm⁻¹ (Fig.2). It is observed, that the FTIR shows two

main frequency bands near $582.78 - 567.01 \text{ cm}^{-1}$ (ν_1) and the second frequency band near $435-445 \text{ cm}^{-1}$ (ν_2) (Table 1). These two observed bands ν_1 and ν_2 correspond to the intrinsic vibrations of tetrahedral and octahedral $\text{Fe}^{3+} - \text{O}^{2-}$ complexes, respectively(15).

Table I. Lattice parameter (a), Crystallite size (t), Interplanar distance (d) and IR frequency bands (ν_1, ν_2):

Composition of $\text{Mg}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$	a (\AA)	t (nm)	d(nm) (311)	$\nu_1(\text{cm}^{-1})$ $\nu_2(\text{cm}^{-1})$
X= 0.0	8.3943	43.7	0.2531	582.78 445.0
X= 0.5	8.3583	53.9	0.2520	597.25 435.86
X= 1.0	8.3688	50.82	0.2523	567.01 436.03

3.3 Morphology by SEM

The morphology of prepared ferrite samples was studied using SEM technique. The SEM images of The samples were shown in Fig. 3. These show that the particles have an almost homogeneous distribution and some of them are in agglomerated form. The micrographs show the grainy structure with clusters of fine particles.

4. Conclusion

Nanocrystalline $\text{Co}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ (x=0.0,0.50 and 1.0) ferrite samples were successfully prepared by the sol gel auto combustion technique using citric acid as a fuel. X-ray diffraction pattern confirms the formation of single phase cubic spinel structure. The crystallite size of the Mg-Co ferrites was in the range of 50-69 nm. SEM micrographs of all the samples indicate the morphology and FTIR confirms the presence of intrinsic vibrations of tetrahedral and octahedral $\text{Fe}^{3+} - \text{O}^{2-}$ complexes, respectively.

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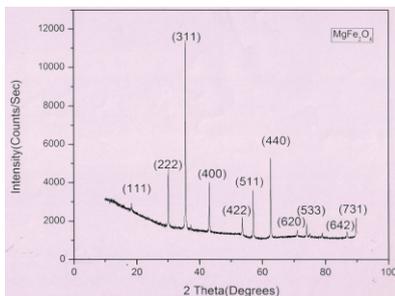


Fig1.(a) X-ray diffraction pattern of MgFe_2O_4

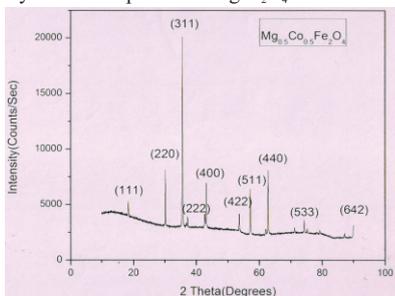


Fig1.(b) X-ray diffraction pattern of $\text{Mg}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$

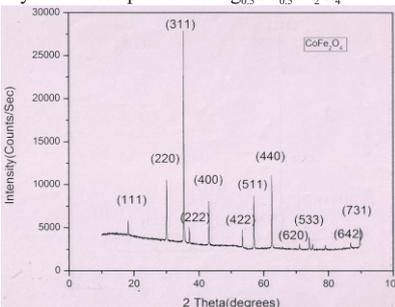


Fig1.(c) X-ray diffraction pattern of CoFe_2O_4

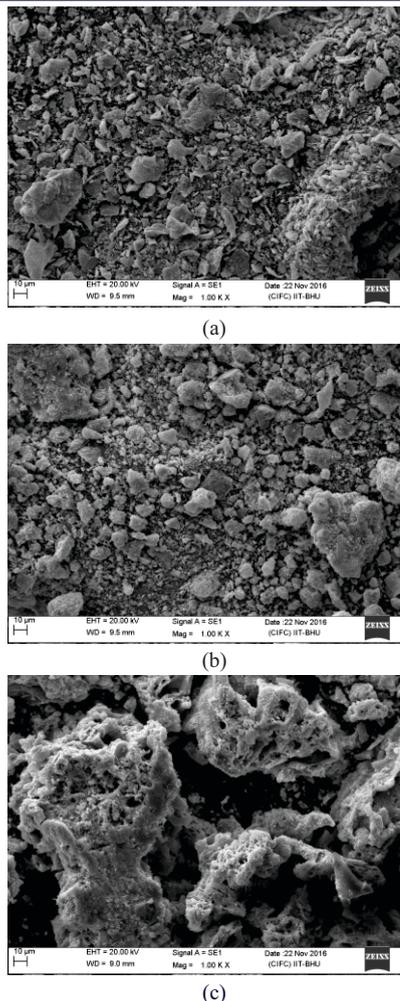


Fig.3 Scanning electron micrographs of $\text{Mg}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ a)x=0, b)x=0.5, c)x=1.0

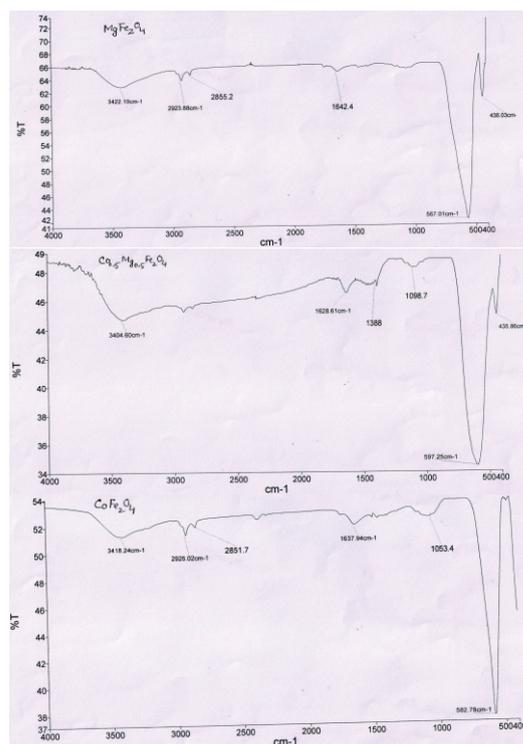


Fig.2 FTIR spectra of $\text{Mg}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles

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