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Structural, dielectric and magnetic properties of cobalt ferrite prepared using auto combustion and ceramic route

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A B S T R A C T

Cobalt ferrite is synthesized by using low temperature auto combustion and high temperature ceramic methods. The prepared samples have values of lattice constant equal to 8.40 Å and 8.38 Å for auto combustion and ceramic methods respectively. The FTIR spectrum of samples of the auto combustion method shows a high frequency vibrational band at 580 cm^{-1} assigned to tetrahedral site and a low frequency vibrational band at 409 cm^{-1} assigned to octahedral site which are shifted to 590 cm^{-1} and 412 cm^{-1} for the ceramic method sample. SEM micrographs of samples show a substantial difference in surface morphology and size of the grains between the two methods. The frequency dependent dielectric constant and ac conductivity of the samples measured from 1 Hz to 2 MHz at room temperature are reported. The room temperature magnetic hysteresis parameters of the samples are measured using VSM. The measured values of saturation magnetization, coercivity and remanent magnetization are 42 emu/g, 1553 Oe, 18.5 emu/g for the auto combustion method, 66.7 emu/g, 379.6 Oe, and 17.3 emu/g for the ceramic method, respectively. The difference in preparation methods and size of the grains causes interesting changes in electrical and magnetic properties.

1. Introduction

Spinel ferrites with general formula MFe_2O_4 (M=Co, Ni, Zn, or other metals) are well known as they continue to be one of the most important scientific and industrial materials by virtue of their electrical and magnetic properties [1]. Among them, cobalt ferrite is a well-known inverse spinel structured hard magnetic material with high coercivity, moderate magnetization and highest magneto-crystalline anisotropy [2,3]. It has Co^{2+} ions in B site, Fe^{3+} ions distributed in A and B sites equally [4]. It has been reported the properties of ferrites are sensitive to method of preparation and post sintering process [5,6]. Ferrites are prepared using several methods such as co-precipitation, flash combustion, citrate precursor, sol–gel and ceramic techniques. Conventionally ceramic method has been a well approved method for the synthesis of ferrites. Recently researchers focus on the auto combustion method. This method is preferred as it yields ferrite samples with good chemical homogeneity, high purity and crystallinity [7]. An improvement is made over the conventional auto combustion method without using external water in the precursor stage which is reported as novel combustion route [8,9]. It is claimed in the novel combustion method that the ferrite samples are free from water born impurities and have fine particle size of narrow distribution. In the present work, the improved novel combustion route is employed for the synthesis of cobalt ferrite. To have a direct comparison of impact of nano size of particles, cobalt ferrite is also synthesized using the ceramic method and studied parallely for the structural, dielectric and magnetic properties of the samples with respect to the preparation methods.

2. Experimental

2.1. Synthesis of cobalt ferrite using auto combustion route

Required amount of cobalt nitrate, ferric nitrate and citric acid are taken in a beaker as starting materials and mixed magnetically to obtain a homogeneous mixture. The precursor mixer in the form of gel is heated on a hot plate under constant stirring at temperature of about (80–90) °C to remove inherent water present. The dried gel is heated on a hot plate until self ignited. The entire preparation processes completed within 30 min. The final product is annealed at 300 °C for 1 h to remove the volatile compound present in the final product. The procedure of synthesis reported here involves low temperature, short duration and less cost over the similar methods reported earlier [10].

2.2. Synthesis of cobalt ferrite using ceramic route

Oxides of cobalt and iron are taken in stoichiometric ratio and ground in a mortar and pestle for 1 h. The homogeneous mixture

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is subjected to pre sintering in air at 1100 °C for 15 h and furnace cooled at a rate of 100 °C per hour. The product is ground, pelletized and post sintered at 1150 °C for 8 h and furnace cooled.

Hereafter, the synthesized $CoFe_2O_4$ particles using auto combustion and ceramic routes are termed as $CoFe_2O_4$-A and $CoFe_2O_4$-B respectively.

2.3. Characterization

Structure of $CoFe_2O_4$ powder is identified using X-Ray Diffraction (XRD) study in PANalytical X'pert PRO diffractometer. The diffraction pattern recorded using Cu-Kα_1 radiation with the wavelength of 1.5406 Å. Fourier Transform Infrared (FTIR) spectra is observed using a Shimadzu-8700 FTIR spectrometer over the range of 1200–400 cm^{-1} at room temperature. Surface morphology of the samples is analyzed using Scanning Electron Microscope (SEM) – Hitachi S-3400 N. Dielectric measurements are carried out over the frequency range of 1 Hz to 2 MHz using Broadband Dielectric Spectrometer (BDS) – Novocontrol Technologies-Concept-80. Magnetic properties are investigated using Vibrating Sample Magnetometer (VSM) Lakeshore VSM-7410. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Structural and morphological analysis

3.1.1. X-ray diffraction study

The room temperature XRD patterns of $CoFe_2O_4$ samples obtained from both the synthesis routes are shown in Fig. 1. The XRD patterns of the samples conform with JCPDS no. 22-1086 for cobalt ferrite. The crystallite size is calculated using Scherrer's formula [11] for $CoFe_2O_4$-A.

$$D = 0.9\lambda/\beta \cos\theta \tag{1}$$

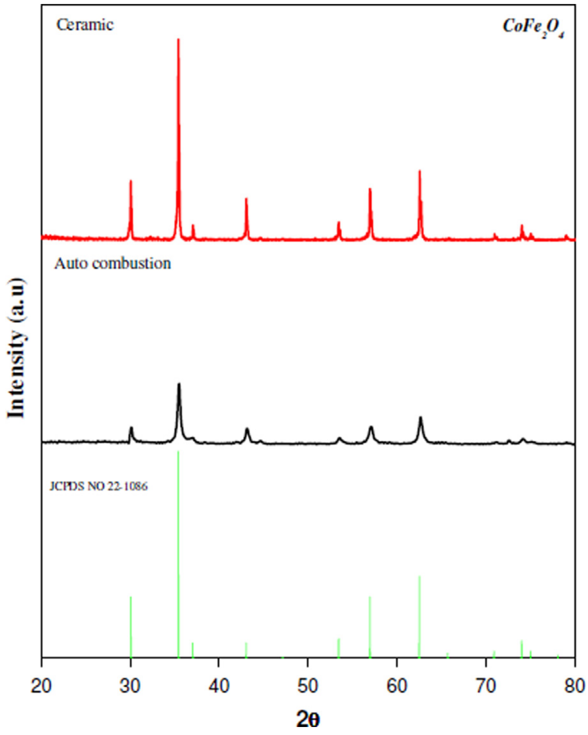

Fig. 1. XRD pattern of $CoFe_2O_4$ prepared using auto combustion and ceramic route.

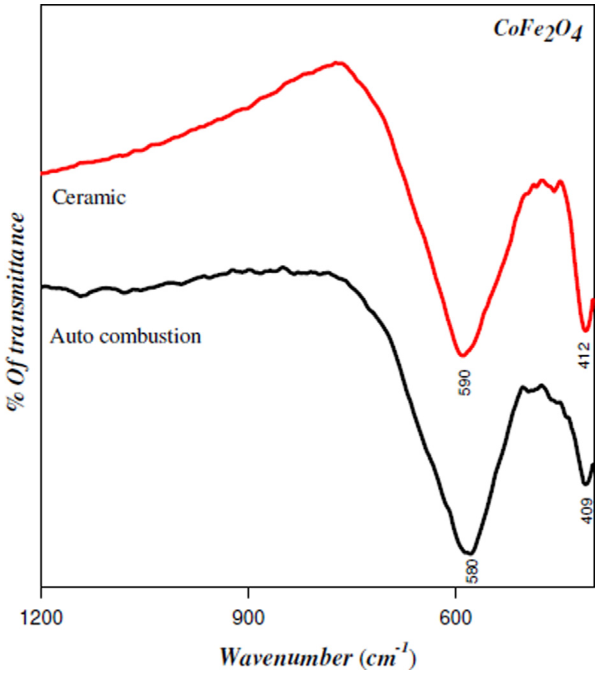

Fig. 2. FTIR spectrum of $CoFe_2O_4$ prepared using auto combustion and ceramic route.

here, D is crystallite size, λ is X-ray wavelength, β is full width at half maximum and θ is Bragg angle. The size of the crystallite is 28 nm for $CoFe_2O_4$-A and that of $CoFe_2O_4$-B is 301 nm samples. Lattice constant calculated using the following relation:

$$a = \frac{\lambda}{2}\left[\frac{h^2+k^2+l^2}{\sin^2\theta}\right]^{1/2} \tag{2}$$

here, a is lattice constant, λ is wavelength, and hkl are Miller indices. The calculated value of lattice constant is 8.40 Å for $CoFe_2O_4$-A and 8.38 Å for $CoFe_2O_4$-B. The variation in the lattice constant is attributed to the change in the kinetics of the reaction methods which may alter substantially site occupancy of cations in A and B sites of cobalt ferrite and nature of cations [5].

3.1.2. FTIR analysis

The infrared spectra of samples observed at room temperature are shown in Fig. 2. Two persistent and characteristic absorption bands are found in the range of frequency from 590 to 409 cm^{-1}. The frequencies of IR bands are in agreement with the report of Waldron [12] for similar ferrites. In ferrites the metal ions are situated in two different sub-lattices designated as tetrahedral (A) and octahedral (B) sites. The stretching of these geometrical configurations is attributed to the band at around 600 cm^{-1} for tetrahedral group and 450 cm^{-1} for octahedral group. The information about the presence of tetrahedral and octahedral coordination confirms the formation of spinel structure. The FTIR spectrum of samples of the auto combustion method shows a high frequency vibrational band at 580 cm^{-1} assigned to tetrahedral site and a low frequency vibrational band at 409 cm^{-1} assigned to octahedral site which are shifted to 590 cm^{-1} and 412 cm^{-1} for the ceramic method sample. It is noticed that the vibrational frequencies are shifted to the low frequency region for $CoFe_2O_4$-A when compared with $CoFe_2O_4$-B. The shift in frequency occurs due to change in bond length between the ions in their coordinated structures [13].

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