Microstructural, morphological and electrical properties of sol-gel derived CoFe$_2$O$_4$ nanomaterials

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Abstract. CoFe$_2$O$_4$ nanomaterials have been synthesized through conventional sol-gel process by using CoCl$_2$.6H$_2$O and FeCl$_3$ as precursors and citric acid is used as a capping agent. The as synthesized nanomaterials have been investigated thoroughly using x-ray diffraction (XRD) technique, scanning electron microscopy (SEM) and an impedance analyzer. The XRD patterns indicate the formation of body centered cubic spinel CoFe$_2$O$_4$ having cell constant 8.403 Å and the corresponding space group is Fd-3m, in which the Fe$^{3+}$ and Co$^{2+}$ ions occupied in octahedral and tetrahedral sites in the crystallographic orientations. The average crystallite size was found to be 30 nm. The SEM micrographs reveal that the synthesized nanomaterials (NMs) formed as octahedron and tetrahedron and the particles are well dispersed and contain some pores. We found 17.5% porosity of the nanomaterials that plays an important role in technological applications, e.g. water and chemical filtration related to bio-medical applications. Measurement of the AC electrical properties shows that dielectric constant increases up to 5.13 for 0.3 MHz and then it decreases with increasing applied frequency. Lower dielectric constant at high frequency region appears due to decreasing interfacial polarization and limiting grain boundary effect.

1. Introduction

Generally, magnetic metals and metal oxides have a lot of attraction in materials science and engineering due to their wide range of applicability and outstanding properties. The cobalt ferrite nanomaterials (NMs) are used in various applications and have many efforts because of their unique physical and chemical properties such as low dielectric constant, high electrical resistance as well as excellent chemical stability and mechanical hardness [1-4]. The cobalt ferrite NMs has cubic spinel structure and its properties are affected by composition and microstructure cause of octahedral and tetrahedral occupancy in the lattice sites. For these properties cobalt ferrite is technologically important and suitable for high density recording media [2-3], Ferro fluid technology, biomedicine, magnetic resonance imaging, biosensors, magnetic hyperthermia therapy [4-5], data storage, magnetic refrigerators and microwave devices. These applications are strongly affected by shape and size of the NMs, hence the control of the shape and size of the NMs are quite important. Different types of chemical routes have been used to synthesize the CoFe$_2$O$_4$ NMs such as sol-gel method [6-8], micro emulsion, co-precipitation method [9], polyol reduction method [10], laser ablation, Turkevitch method and transmetallation technique [9] etc. Among these methods, we used sol-gel method for the synthesis of CoFe$_2$O$_4$ NMs because it is cost-effective and low temperature operation and an excellent chemical route for obtaining fine nanocrystalline and homogeneous powder.

In this work, to synthesis CoFe$_2$O$_4$ NMs through sol-gel route, ferric chloride and cobalt chloride are used as a precursors and citric acid as a capping agent. We have studied the effect of annealing...
temperature on its structural properties through XRD technique. The surface morphologies, chemical composition and AC electrical properties have also been examined for sample annealed at 600 °C.

2. Experimental Procedure
In order to synthesize the CoFe$_2$O$_4$ NMs using a citrate assisted sol-gel route stoichiometric amounts of 1.19 g CoCl$_2$, 6H$_2$O (97%; Merck), and 0.82 g FeCl$_3$ (98%; Merck) dissolved in 200 ml distilled water and a few drops of concentrated nitric acid were also added to prevent hydrolysis. Then, 8.46 g citric acid and a few ml of dimethylamine were also added to prevent the agglomeration of the particles. Thereafter, the mixtures of the solution were magnetically stirred at 60 °C for 2 hours and then evaporated at 100 °C to form a gel. The gel mixtures were dried at 150 °C for 18 hours and the resulting powder was decomposed in air and heated at 250 °C for 3 hours inside a furnace at air ambient. The powder samples were ground thoroughly about 2 hours using an agate mortar pestle and heat treated further at different temperatures for 4 hours at air ambient. Structural features such as crystallite size and crystallographic structure were studied for different annealed temperatures of the as synthesized NMs using Rigaku Smart Lab X-ray diffractometer using Cu-Kα radiation of λ = 1.54184 Å. The surface morphological properties were examined through a field emission scanning electron microscopy (FE-SEM) with accelerating voltage 5 keV (Philips XL30 FEG). The atoms present in the NMs composition and the ratio of the atoms were confirmed by energy dispersive x-ray (EDAX) intensity.

3. Results and Discussion
3.1. Structural Characterization
Figure 1 shows the XRD patterns of the as synthesized CoFe$_2$O$_4$ NMs annealed in air at temperatures 400 °C, 600 °C, 700 °C, 800 °C and 900 °C, respectively. It is seen from figure 1 that the observed peaks (220), (311), (222), (400), (422), (511) and (440) are the indication of spinel CoFe$_2$O$_4$ body centred cubic structure with space group Fd-3m (227), having lattice parameter ‘a’ is equal to 8.403 Å (JCPDS card: 22-1086) [2, 6-8]. In the spinel structure, the cations Co$^{2+}$ and Fe$^{3+}$ may be occupied into two different sites, i.e. octahedral and tetrahedral sites within the lattice structure [2, 10]. The average crystallite size was determined from XRD peak broadening using the Debye-Scherrer formula [12],

$$D = \frac{K \lambda}{\beta \cos \theta}$$

where, λ is the wavelength of the x-ray radiation, K is a constant (0.94), β is the full width at half maximum in radian, θ is the diffracting angle. The average crystallite size was found to be 30 nm. Besides, the peaks around 20 = 44° and 65° indicate trace amount of FeCo alloy formation in the composition [9-10, 13]. The FeCo phases were observed with body centred cubic structure with space group Pm-3m. The lattice parameter ‘a’ is equal to 2.954 Å. Moreover, at 400 °C the impurity phases of hematite (Fe$_2$O$_3$) and cobalt oxide (Co$_3$O$_4$) were confirmed from XRD patterns, which also reduces at 600 °C [6, 9-10]. The average crystallite size becomes larger with increasing annealing temperatures and the impurity phases were also reproduced due to decomposed of NMs. Thus, the optimal temperature to synthesize the CoFe$_2$O$_4$ NMs is 600 °C.
Figure 1. X-ray diffraction patterns of the as synthesized CoFe$_2$O$_4$ nanomaterials.

3.2. Surface Morphologies
Figure 2 shows the SEM micrographs of the as synthesized cobalt ferrite NMs for samples annealed at 600 °C. It is seen from the SEM micrographs in figure 2 that the synthesized NMs are formed as octahedron and tetrahedron and the particles are well dispersed and the mean particle size is about 30 nm [7]. The microstructure of the synthesized NMs reveals the grains are perfectly ordered with porous structure. The porosity was determined using the formula, $P = 1 - (\rho_m/\rho_x)$, where, $\rho_m$ and $\rho_x$ are measured density and x-ray density of the NMs, respectively [14]. The porosity of the NMs was found to be 17.5%.
The compositional analysis of the CoFe$_2$O$_4$ NMs was performed through EDAX analysis. It is seen from figure 3 that the ratio of Fe and Co atoms are 49.37% and 50.63%, respectively. It is important to notice that the EDAX analysis shows the ratio of Fe and Co is very close to 50:50 (1:1) which is in good agreement with nominal composition.

![SEM micrographs of the as synthesized CoFe$_2$O$_4$ NM samples annealed at 600 °C.](image1)

**Figure 2.** The SEM micrographs of the as synthesized CoFe$_2$O$_4$ NM samples annealed at 600 °C.

| Element | Wt% | At% |
|---------|-----|-----|
| FeL     | 48.03 | 49.37 |
| CoL     | 51.97 | 50.63 |
| Matrix  | Correction | ZAF |

![EDAX spectra of the as synthesized CoFe$_2$O$_4$ nanomaterials.](image2)

**Figure 3.** The EDAX spectra of the as synthesized CoFe$_2$O$_4$ nanomaterials.

### 3.3. AC Electrical Properties

The AC electrical properties were measured using an impedance analyser at room temperature. Figure 4 shows the dielectric constant, k and capacitance, C as a function of frequency for the cobalt ferrite NMs. The dielectric properties of materials are affected by synthesis technique, temperature, percentage of composition, density, crystal structure, porosity and heat treatment, etc. In an ac fields,
The dielectric constant is a complex quantity and we measured the real part of this quantity as a function of frequency. The dielectric constant is increased steeply with the increasing of frequency up to 0.2 MHz and holds maximum value 5.13 at 0.3 MHz, and then it decreases with increasing applied frequency. This results indicate the dielectric relaxation at low frequency to dispersion phenomenon at high frequency [2].

![Graph](image)

**Figure 4.** The dielectric constant and capacitance of the as synthesized samples annealed at 600 °C.

According to Maxwell–Wagner model, the grains are separated by poorly conducting grain boundaries [15]. At first, the dielectric constant increases due to increasing polarization with applied frequency. After certain high frequency, the electron cannot keep up with the applied field, i.e. electrons change their direction that decreases the probability of electrons to reach the grain boundaries. The grain boundaries weaken at higher frequencies. As a result, the polarization decreases and hence also the dielectric constant. Besides, from figure 4, it is seen that the capacitance of the cobalt ferrite NMs decreases with increasing frequency due to diminishing grain boundary effect [2, 13].

Figure 5(a) illustrates the ac conductivity and ac resistance of the cobalt ferrite NMs and 5(b)
represents the reactance and impedance of the synthesized NMs with applied frequency. The ac conductivity of dielectric materials is influenced by the local electric charge as well as charge hopping process [16]. It is observed from figure 5(a) that the conductivity increases with increasing frequency due to the increasing of the mobility of the electron. From figure 5(b) it is noticed that the behaviours of the impedance are very similar to AC resistance as shown in figure 5(a), which decreases with increasing applied frequency due to decreasing interfacial polarization. The reactance gradually increased with the increasing of frequency, after certain maximum value it falls down due to the limiting grain boundaries of the NMs.

4. Conclusions
The synthesis, microstructural, surface morphological and frequency dependent electrical properties of CoFe$_2$O$_4$ NMs using sol-gel route is explained. The XRD patterns confirm the crystalline phase of the synthesis NMs is spinel CoFe$_2$O$_4$. The SEM micrographs show the CoFe$_2$O$_4$ NMs formed as octahedron and tetrahedron. The synthesized CoFe$_2$O$_4$ NMs contains some pores, that play an important role in water and chemical filtration related to bio-medical applications. The high resistance and low dielectric constant indicate the low eddy loss of current, which make the NMs as a promising candidate for high frequency components.

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