



RESEARCH ARTICLE

EFFECT OF AG DOPED CoFe_2O_4 NANOPARTICLES: PHYSICO-CHEMICAL CHARACTERIZATION AND ELECTRIC PROPERTIES

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ABSTRACT

This work reports, the crystalline Ag doped cobalt ferrite (CoFe_2O_4) spinel oxide powder was synthesized by nitrate-citrate sol-gel auto-combustion process. The study was focused on effect of Ag doped CoFe_2O_4 on the Physico-Chemical characterization and electrical properties. The Phase composition, crystallinity, structure and electrical behaviour materials were studied by X-ray diffraction, FTIR and electric properties. XRD result confirmed the single cubic phase spinel structure with the lattice constant is obtained in the range of 8.367 to 8.377 Å. FTIR analysis confirmed the two specific vibrational stretching bands corresponding to the spinel ferrite geometry. The DC electrical resistivity is obtained 1.4 to 1.8 cm at room temperature. Dielectric parameters were studied as a function of frequency in the range of 1–10 MHz at 300 K.

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INTRODUCTION

The study and application of nanomaterials has grown in recent years because a nano-sized object exhibits different properties of its bulk materials due to changes in its surface-volume ratio. Among the many nanomaterials, transition type metal oxide based materials are gaining more attention by researchers due to a wide range of broad spectrum of applications such as medical, energy storage, fabrication of advanced devices. Because of their remarkable electrical and magnetic properties which are not found in any other magnetic material. Most popular type of ferrite is the cubic spinel structure which has tetragonal [A] sites and octahedral [B] sites in the AB_2O_4 crystal structure. The basic electrical and magnetic properties of ferrite are easy to control as they depends on the method of preparation and variation of compositions and cation distribution. The high permeability in radio frequency region, high electrical resistivity mechanical hardness chemical stability, reasonable cost and easy preparation are the important feature of spinel ferrite. Ferrites represent an important category of magnetic material, which are great demand due to their numerous practical applications. According to the literature cobalt ferrites is random spinel structure with Co^{2+} ions going to tetrahedral (A) and octahedral [B] sites therefore, it will be interesting to investigate the various properties of cobalt ferrite.

The detailed study of structural, morphological, magnetic and electrical properties of the cobalt spinel ferrite has not been investigated in the literature.

Experimental Details

The cobalt ferrite nanoparticles having the generic chemical formula CoFe_2O_4 were synthesized by sol-gel auto combustion technique at a very low temperature (180°C) using the below mentioned raw materials.

Raw Materials were:

Cobalt Nitrate - 99% Pure (AR Grade) ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
Silver Nitrate-99% Pure (AR Grade) ($\text{Ag}(\text{NO}_3)$)
Ferric Nitrate - 99% pure (AR grade) ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)
Citric acid - 99% pure (AR grade) ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$)
Ammonia - 99% pure (AR grade) (NH_3)

The Ag doped CoFe_2O_4 nanoparticles were synthesized by sol-gel auto combustion method using citric acid as a fuel. The stoichiometric proportion of metal nitrates to fuel was taken as 1:3. The used reagents were stirred into separate glass beakers for 30 min to dissolve completely into distilled water. After complete dissolution they were mixed together and stirred till we get homogeneous solution. The drop-by-drop ammonia solution was added to adjust the pH of the mixed solution at 7. Further, the solution was continuously stirred and heated at 90°C on a hot plate with magnetic stirring. On the formation of sol-gel, very viscous gel the temperature was further raised up to 120°C so that the ignition of the gel started and finally the loose powder was obtained. The as-burnt powder was ground in Agate Mortar and Pestle to get a fine ferrite powder. Finally

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the burnt powder was calcined in air at 500 °C temperature for 5hrs and cooled to room temperature.

Characterizations:

The crystalline phase of sintered cobalt ferrite nanoparticles were observed by using powder XRD Cu-K α radiation ($\lambda=1.540$ Å) at room temperature. The temperature of the sample is measured using a calibrated chromel - alumel thermocouple. A ferrite sample in the form of pellet is fixed to the soft iron piece and introduced into the furnace. The position of pellet is confirmed with the help of the mirror. The temperature of the sample is increased slowly by gradually increasing the current in the heating coil with the help of a dimmer stat. The temperature at which the ferrite sample loses its magnetization and drops is measured with the help of thermocouple.

3. RESULTS AND DISCUSSIONS

3.1 X-ray analysis

X-ray diffraction spectra were carried out to authorize single phase nano-crystalline nature of Ag doped CoFe_2O_4 nanocrystals as revealed in Fig. 3.1. The XRD patterns consist of prominent diffraction (hkl) planes, i.e., (220), (311), (222), (400), (422), (511), (440), and (533) belonging to the establishment of cubic spinel geometry and well analogous with the typical data from the JCPDS card #221086. No supplementary and transitional phase was detected in the XRD spectra. According to the literature, Ag doped CoFe_2O_4 has an inverse spinel geometry which comprises all Co^{2+} ions in octahedral [B] site, and Fe^{3+} ions are equivalently dispersed among tetrahedral (A) and octahedral [B] occupancy sites. The analysis of X-ray diffraction pattern Ag doped CoFe_2O_4 nanoparticles was found to be tetragonal. The 'd' spacing for each peak was calculated using Bragg's law.

$$n\lambda = 2d\sin\theta \quad (1)$$

=

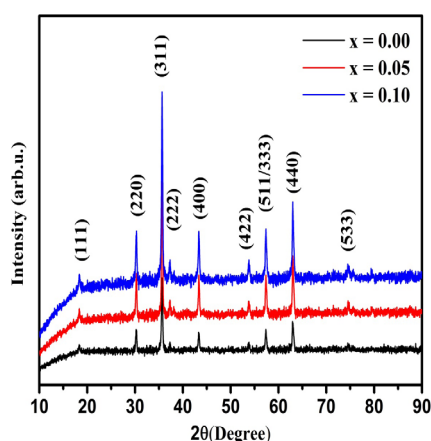


Fig 3.1: XRD pattern of Ag doped CoFe_2O_4

Lattice constant

Using the interplanar spacing 'd' values and corresponding Miller indices, the lattice constant was calculated using the relation

$$a = d_{hkl} (h^2 + k^2 + l^2)^{1/2} \quad (2)$$

where, (h k l) are Miller indices of each plane. The value of

lattice parameter 'a' is given in Table 3.1.

X-ray density

The theoretical density (d_x) is the X-ray density, calculated according to the relation

$$d_x = \frac{ZM}{N_a a^3} \quad (3)$$

Where, z is number of molecules per unit cell ($Z=8$ for spinel ferrite),

M is the molecular weight,
 N_a is Avogadro's number and
 a is lattice constant.

Crystalline size

The crystalline sizes were determined using by Scherrer's formula. The highest intensity peak (311) of the XRD pattern was considered for the determination of full width at half maximum (FWHM). The crystalline sizes are found to be 38 to 44 nm. It can be observed that the crystallite size is increasing with increase in Ag content. The reason behind is the higher mobility of cations and change in strain induced during the sintering process which causes small change in 2θ positions and broadening of the peaks which finally results in the increased crystallite sizes as tabulated in table 4.1.

Table 4.1: Lattice parameters unit cell volume (V), X-ray density (d_x) and particle size (t) for Ag doped CoFe_2O_4

x	a (Å)	d_x (gm/cm 3)	d_p (nm)	P (%)	D (nm)
0.00	8.367	5.291	3.638	31.847	38
0.05	8.372	5.197	3.617	32.656	41
0.10	8.377	5.085	3.587	33.413	44

3.2. FTIR Studies

The FTIR spectra of the produced spinel ferrites are displayed in Fig. 3.2. The FTIR spectra demonstrate dual chief absorption bands ν_1 and ν_2 those are shifting to the lower wavenumber direction. The first absorption band appears in the vicinity of 380–410 cm^{-1} and second absorption in the scope of 520–580 cm^{-1} . The appearance of two major bands corresponds to the vibrational modes of the entire spinel compounds, approving the construction of the metal oxides. As displayed in Fig. 3.2 the bands at 396 cm^{-1} and 542 cm^{-1} represent the vibrations of octahedral metal–oxygen–stretching Fe–O bonds and the peaks at 540.26 cm^{-1} and 370.12 cm^{-1} represent the vibrations of tetrahedral metal–oxygen (-M–O), stretching Co–O bonds. The shifting of the frequencies to higher side is a clear evidence of the displacement of Fe^{3+} ions from octahedral site to tetrahedral site. The substitution of bigger ions of Ag^+ by replacing Fe^{3+} has resulted in the enlargement of the unit cell which is evident from the increase of the lattice parameter.

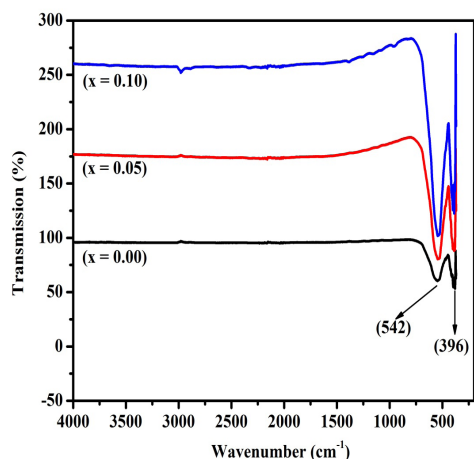


Fig 3.2: FTIR spectra for Ag doped CoFe₂O₄

3.3. Electrical Properties

The variance in the DCR v/s temperature (323K – 723K) for sample has appeared in Fig. 3.3. As it reflects that the resistivity liberally diminishes with increment in temperature because of the hopping of electrons, which shows the semiconductor nature. Verwey and Boer’s system can clarify the conduction procedure in Ag doped CoFe₂O₄ samples. In the current investigation, the plot of log ρ v/s 1000×T⁻¹ shows the change in slope, which makes two straight lines or areas to be a specific ferromagnetic locale [11-15]. The variation in resistivity as a function of temperature obeys Arrhenius relation. Using DCR plots, the activation energy ΔE for each sample in the ferri-magnetic and para-magnetic locale was determined. ‘Activation energy ΔE’ estimations of the samples under scrutiny are observed to in a set of 0.42 eV.

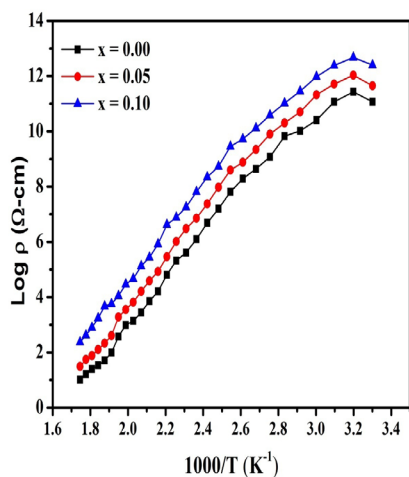


Fig.3.3. The temperature dependent DC Resistivity of Ag doped CoFe₂O₄

3.4. Dielectric properties.

Fig. 3.4 and 3.5 represents the frequency dependence of dielectric constant (ε') and dielectric loss (tanδ) for different concentration samples sintered from 400°C for 5 h in the frequency range from 20 Hz to 2 MHz at room temperature.

The ε' decreases with increasing frequency and the decreasing trend becomes slow in higher frequency region, showing frequency dispersion at low frequency range. This behavior is normal for the polar dielectric materials [28]. The decrease in ε' can be explained by Maxwell-Wagner type and it is consistent with Koop’s theory of dielectrics [4, 28, 29]. According to the Koop’s theory of dielectrics, the dielectric structure is composed of conducting grains and insulating grain boundaries [28-29]. The grain boundaries are formed due to the oxidation of crystallines or superficial reduction during sintering process in porous ferrite materials. When the dielectric material is placed over the alternating field, owing to the hopping of electrons inside ferrites, electrons arrive at the grain boundaries, accumulating at the grain boundaries due to high grain boundary resistance. This process is called as space charge polarization [30-33]. At lower frequencies, the effect of grain boundaries dominates over grains and the space charge polarization occupies major status. Thus, the ε' is high. However, at higher frequencies, owing to the weakly space charge polarization and electrons cannot follow the changes of the applied field, the ε' decreases and then becomes a constant value beyond a certain frequency limit. Fig.3.6 shows that there is a relaxation in tanδ for all the samples at low frequency region [34-36]. The Ag ion doped in CoFe₂O₄ for Fe³⁺ ions was effective in decreasing the dielectric loss in fig 3.5.

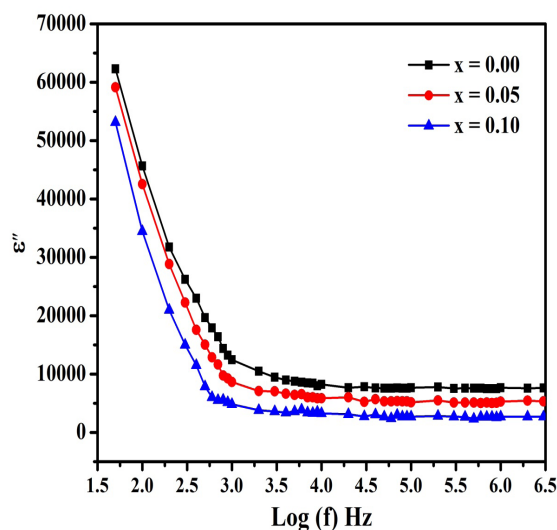
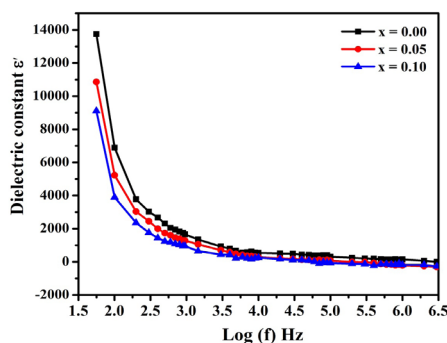


Fig 3.5. Variation of Dielectric loss with frequency dependent of Ag doped CoFe₂O₄

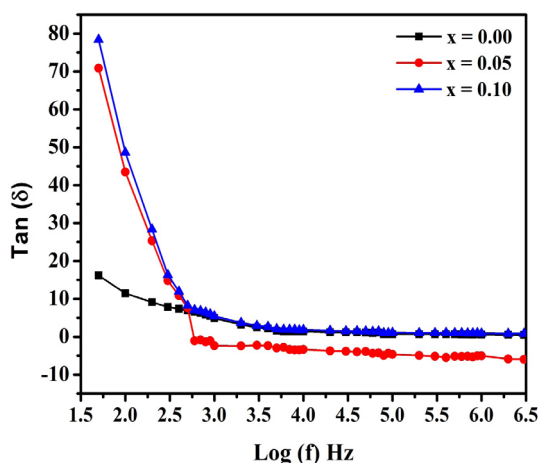


Fig 3.6. Variation of $\tan (\delta)$ with frequency dependent of Ag doped CoFe_2O_4

CONCLUSIONS

The reported work concludes the preparation of Ag⁺ substituted CoFe_2O_4 nanoparticles using sol gel auto-combustion method. X-ray diffraction results showed the formation of single phase tetragonal spinel structure. The crystallite size confirms the nanocrystalline nature of the samples. All the structural parameters such as lattice constant, X-ray density etc were in the reported range. While the FTIR analysis of the ferrites confirm the formation of spinel phase as well as the successful substitution of the Ag⁺ ions within the ferrites. The DC electrical resistivity decreases as the temperature increases, implying the semiconducting behavior of the fabricated in Ag doped CoFe_2O_4 nanoparticles. In addition, the DC electrical resistivity was observed to be enhanced with an increase in the Ag ion substitution. All the dielectric parameters decline with an increase in frequency, corresponding to the Verwey and Bohr's model.

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