

Substitution of La^{3+} in $\text{Cu}_{0.5}\text{Co}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0.02, 0.06$) Spinel Ferrites Improves the Structural and Dielectric Properties

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Abstract

Nanosized Spinel ferrites with composition $\text{Cu}_{0.5}\text{Co}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0.2, 0.6$) synthesized by Sol-Gel auto Combustion method. The prepared sample was calcinated at 800°C for 4 hours. The substitution of La^{3+} effects the structural parameters, which is characterized by X-ray diffraction (XRD). The X-rd analysis shows that the crystallite size is 34.609 nm for 0.02 and 38.994 nm for 0.06 was calculated by using Debye-Scherrer's formula. dislocation density shows at value 8.3485 1/m^2 & 6.5765 1/m^2 . Hopping length at tetrahedral and octahedral sites (L_A and L_B). 3.6308 \AA and 2.9645 \AA for $x=0.02$ 3.6143 \AA and 2.9510 \AA for $x=0.06$ The variation of dielectric constant (ϵ') as a function of frequency in a range of 100Hz to 1MHz was studied. Nanosized spinel ferrites $\text{Cu}_{0.5}\text{Co}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.2, 0.6$) were synthesized via the sol-gel auto-combustion method and calcinated at 800°C . XRD confirmed structural changes with La^{3+} substitution, showing crystallite sizes of $\sim 35\text{--}39 \text{ nm}$ and corresponding dislocation densities. Hopping lengths at tetrahedral and octahedral sites varied with La content. Dielectric constant behavior was analyzed across $100 \text{ Hz--}1 \text{ MHz}$.

Keywords: Sol-Gel auto combustion method, X-rd, dislocation density, hopping length, dielectric

INTRODUCTION

Spinel ferrites, ferrimagnetic oxides, are acquiring importance as magnetic materials due to their high electrical resistivity, low eddy current losses, and suitable dielectric loss.

There are two types of spinel ferrites: soft and hard. With potential applications in medical, storage, electronics, optoelectronics, microwave, and electromagnetic devices, soft spinel ferrites AFe_2O_4 (A = metal ions) have made substantial contributions to scientific and technological innovations [1,2,3,4,5]. In spinel ferrites, the electric and magnetic properties can be changed by the locations of different metal ions at A on tetrahedral & B on octahedral sites [6,7].

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The doping of rare earth ions in spinel ferrites changes the structure and texture of nano spinel ferrite compounds [8,9]. In the present paper, we discuss an attempt to enhance the structural and dielectric characteristics of Cu-Co spinel ferrites prepared by the Sol-gel auto-combustion process by adding rare earth La^{3+} . Sol-gel auto combustion is one of the common and low cost synthetic techniques and the most effective methods for controlling crystallite size and other material characteristics [10,11].

Synthesis Method

La-doped Cu-Co ferrites were synthesized by Sol-gel auto combustion technique. The empirical

formula is taken as Cu_{0.5}Co_{0.5}Fe_{2-x}La_xO₄ for x=0.02 to 0.06. Ferric nitrate (Fe(NO₃)₃·9H₂O), cobalt nitrate (Co(NO₃)₂·6H₂O), and lanthanum nitrate (LaN₃O₉·6H₂O), copper nitrate (Cu(NO₃)₂·9H₂O) were used as the starting chemical reagents of 99.9% purity in stoichiometric amount and dissolved in 30 ml of double distilled water. After stirring for 30 min, a homogenous solution is formed, which is converted into the gel after the addition of urea. gel was shot into the microwave, resulting in a frothy dark brown powder. The materials were crushed for 2 hours using a mortar pestle. The prepared powder was then calcinated at 800°C in a furnace for 4 hours and cooled slowly at room temperature. These samples are further grinded using a mortar pestle for 2hr to prepare fine powder for characterization.

RESULT AND DISCUSSION

X-rd Analysis

Figure 1. Displays the XRD pattern of Cu_{0.5}Co_{0.5}Fe_{2-x}La_xO₄ (x = 0.02, 0.06) spinel ferrites calcined at 800°C for 4 hours. Both samples shows, FCC (Face centered cubic) spinel structures belonging to the space group; Fd-3m[12]. The XRD pattern's peaks at (220), (311), (222), (400), (422), (511), (440), and (533) confirmed the sample is well crystallized into single-phase cubic spinel structure for x=0.02. and for x=0.06 the impurity phases LaFeO₃ were developed near 33°, 42°, and the value of 2θ for x=0.02 is 35.478 and for x=0.06 is 35.646, which shows the peak (311) slightly shifting due to the ionic radius of Lanthanum (1.03 Å) is greater than Ferric ion (0.64 Å)[13]. The full-width half maximum (FWHM) of the most intense (311) plane was used to calculate the average crystallite size of the nano ferrites produced using Debye's Scherrer equation.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad 1$$

The crystallite size of x=0.02 is 34.609nm and for X=0.06 is 38.994nm. Dislocation density(δ) and particle size(D) are inversely related, affecting the crystalline size. The dislocation density decreases with an increase in La³⁺ ion, hence the Crystalline size increases. Hoping length is the distance between magnetic ions at tetrahedral site radii (L_A) and octahedral site radii (L_B) which are calculated by $L_A = 0.25a\sqrt{3}$, $L_B = 0.25a\sqrt{2}$ [14]. The values of the hoping length at the tetrahedral and Octahedral site radii are shown in Table 1. The tetrahedral site radii are greater than the octahedral site radii.

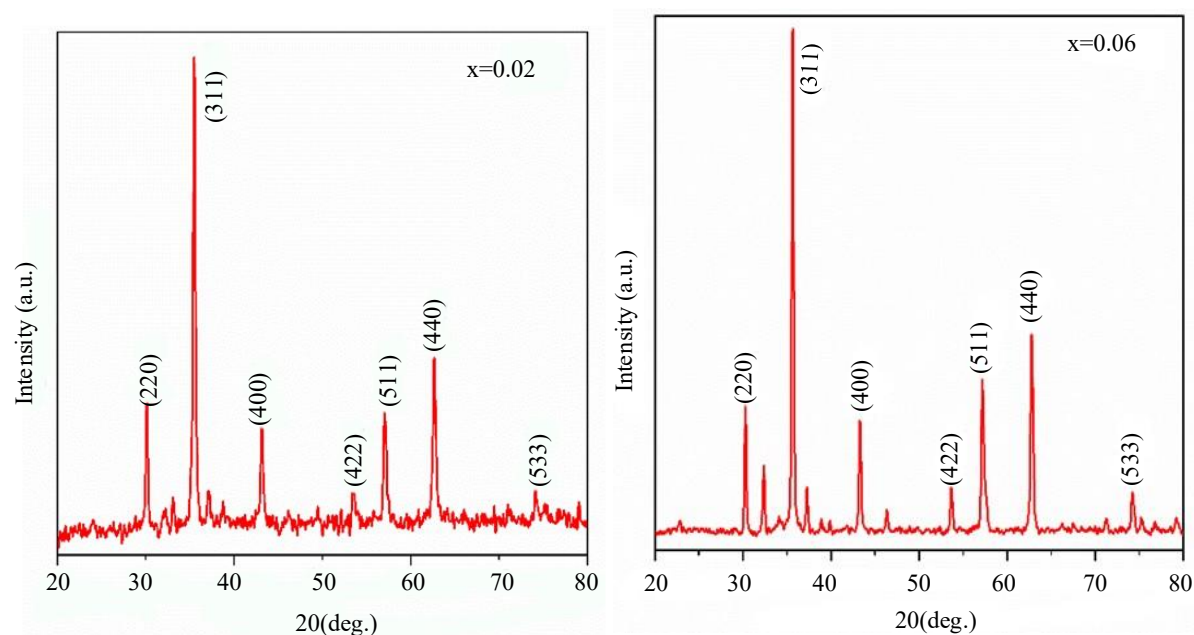


Figure 1. Xrd pattern for x=0.02 and x=0.06 of CuCoLa_xFe_{2-x} Spinel ferrites.

Table 1. 2θ , full-width half maxima (β), d-spacing, Crystallite size(D), Lattice parameter (a), Volume (V), dislocation density (δ), Hopping length (L_A & L_B) of prepared nanoferrites

Sample	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{F}_{1.98}\text{La}_{0.02}\text{Fe}$	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{F}_{1.94}\text{La}_{0.06}\text{Fe}$
2θ	35.478	35.646
β (deg)	0.241	0.214
d-spacing(\AA)	0.252	0.251
D_{nm} (nm)	34.609	38.994
Lattice Parameter (\AA)	8.385	8.346
Volume (cm^3)	0.589	0.581
δ (10^{14}) $1/\text{m}^2$	8.3485	6.5765
L_A (\AA)	3.6308	3.6143
L_B (\AA)	2.9645	2.9510

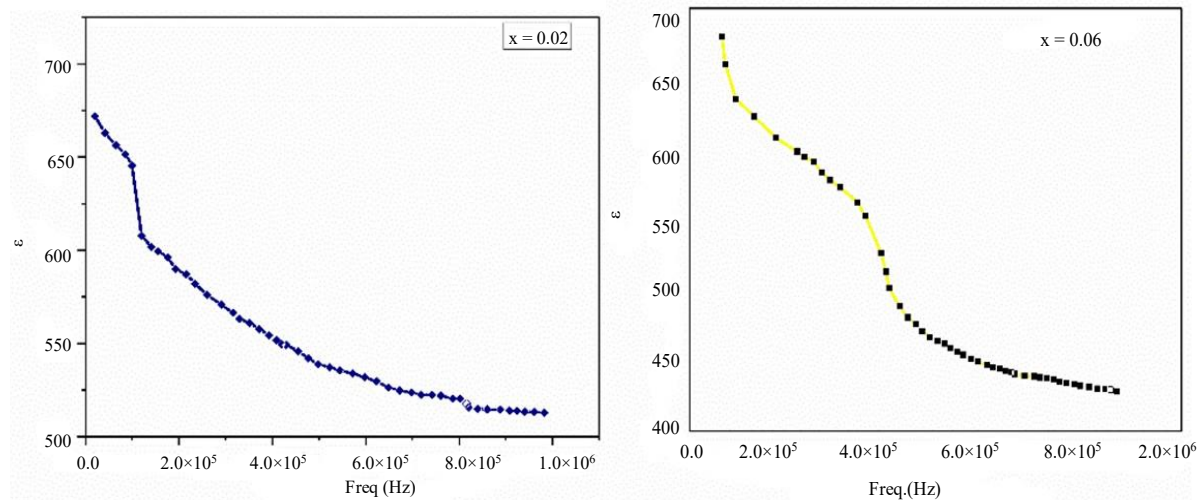


Figure 2. Variation of dielectric constant with frequency for $x=0.02$ and $x=0.06$ of $\text{CuCoLa}_x\text{Fe}_{2-x}$ Spinel ferrites.

Dielectric Study

The frequency dependence of the dielectric constant at constant temperature are shown in Figure 2. The dielectric constant magnitude 671.94, 706.02, for $x=0.02$ & $x=0.06$ in the approximately 100Hz to 1MHz It is observed that at low frequencies, high values of dielectric constant are observed and with increasing frequency, there is decrease in the dielectric constant till it attains a constant value. This behavior with frequency is explained on the basis of Maxwell-Wanger's theory of interfacial polarization that is in agreement with Koops phenomenological theory [14][15]. This hypothesis states that interfacial polarization is more active at low frequencies & with the increasing frequency charges at grain boundaries act as a barrier for the flow of charge carriers causing normal dielectric dispersion which is explained by the grain boundaries[16][17]. At higher frequencies, there is no flow of charge carrier & which is unable to follow the applied electric field, resulting in the loss of polarization & the dielectric approached to a constant value[18].

CONCLUSION

The La^{3+} substituted Cu-Co spinel ferrite synthesized by sol-gel auto-combustion method. The structural properties of the sample were investigated by X-ray diffraction (XRD) and Dielectric properties by an impedance analyser. The crystallite size (D) was found to be increased with the addition of La^{3+} ion in Cu-Co ferrites & dislocation density (δ) decreases, as La^{3+} ion increases. The dielectric constant value decreases with increasing in frequency. This behaviour is explained based on Maxwell-Wanger theory.

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