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Controllable Synthesis of La^{3+} doped $Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{2-x}La_xO_4$ (*x* = 0.0, 0.0125, 0.025, 0.0375, 0.05) nano-ferrites by Sol-Gel Auto-Combustion Route

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Abstract

$Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{2-x}La_xO_4$ (*x* = 0.0, 0.0125, 0.025, 0.0375, 0.05) ferrite powders with uniform distribution of ions and close-packed configuration were prepared via sol-gel auto-combustion route. XRD spectra showed the formation of spinel-phase cubic crystalline structure. SEM results revealed that the irregularity in size and shape of particles increases, and particle distribution uniformity decreases with La^{3+} concentration. Moreover, each curve of the UV-vis spectra revealed two optical energy band gaps. More importantly, DC resistivity (ρ) and the activation energy (ΔE) have minimum values at x=0.0375. The dielectric loss was explained according to Maxwell-Wager space charge polarization. The *P-E* loop showed the ferroelectric nature of the synthesized samples. Moreover, VSM results revealed that the as-prepared samples possessed maximum saturation magnetization (M_S = 56.77 ± 0.0283) and 8-12 GHz operating microwave frequency (ω_m) range at x = 0.0375. All these results show the potential of $Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{1.9625}La_{0.0375}O_4$ ferrite powders for X-band microwave applications.

Highlights

- $Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{2-x}La_xO_4$ ferrite powders via simple sol-gel auto-combustion.
- Crystallite size and lattice constant decrease with increasing La^{3+} cations
- Optical band gap energies and DC resistivity have minimum values at x=0.0375.
- The ferroelectric nature of all the samples was confirmed using the P-E loop.
- Maximum magnetization saturation was observed at $x = 0.0375$.

Keywords: sol-gel auto-combustion; structural; electrical; optical; dielectric; magnetic.

1 Introduction

Spinel ferrites are unique magnetic materials showing semiconductor and ferromagnetic properties and can be regarded as a ceramic or magnetic semiconductor material. Nowadays, these types of magnetic materials are used in different applications, i.e., in high-frequency applications [1], as gas sensors for H_2S [2], for LPG sensing [3], biomedical, and biotechnology [4], optoelectronics applications [5], and removing pollutants as an advanced adsorbent magnetic material from wastewater [6]. Spinel structure oxides have fundamental and practical significance for catalyzes, such as two-phase structure nanowires used as catalytic para-nitroaniline (PNA) to para-phenyl diamine (PPD) reduction reaction [7, 8], lithium-ion batteries [9], magnetic and high-frequency applications [10-13].

The literature indicates that there are numerous conventional and nonconventional routes of preparation, including the solid-state method [14], sol-gel self-igniting route [15, 16], a hydrothermal technique [17], the microemulsion route [18], and the co-precipitation technique [19], which have been successfully used to control the properties of spinel ferrites. The main drawbacks of traditional methods are low reproductivity, the use of high temperature, and contamination problems. In recent years, therefore, novel preparation techniques were developed to meet the current requirements, such as processing efficiency and nanostructure control.

There are numerous studies on the results of Zn [20], Co [21], Cu [22], Zn-Co [23], Co-Cu [24], Cu-Zn [25] and Cu-Co-Zn [15] ferrites. These dopant ions impact on structural, optical, electrical, and magnetic properties of ferrites. According to the best of our survey, there are limited reports on Zn-Co-Cu nano-ferrites powder. Gharagozlou *et al.,* [20] reported low-temperature sintered $ZnFe_2O_4$ soft ferrite synthesized via the Pechini technique. The impact of the calcination temperature on the vibrational and microstructural properties was studied. At 1073 K, the $ZnFe_2O_4$ nano-ferrites saturation magnetization was $M_S = 4.53$ emu/g and the coercivity was $H_C = 47$ Oe. Co-Ferrites ($CoFe_2O_4$) [21] showed two optical band gaps at 4.1 eV, and 4.9 eV using UV-Vis spectroscopy. It was also observed that the resistivity reduced with an increase in temperature [21]. Raja *et al.,* prepared $CuFe_2O_4$ by microwave and sol-gel routes. The comparative studies reported that the magnetic properties depended on the particle size. Cu^{2+} ferrite synthesized by the sol-gel route had a saturation magnetization of 42.23 emu/g. [22].

Татарчук *et al.* developed pure and Zn^{2+} substituted cobalt ferrites with the general formula $Co_{1-x}Zn_xFe_2O_4$ ($0.0 \le x \le 0.5$) through the co-precipitation process. Pure Co^{2+} has a saturation magnetization equal to 91 emu/g, and an optical band gap of 1.17 eV. In contrast, when the concentration of Zn^{2+} is $x = 0.2$, the saturation magnetization (114 emu/g) was at the maximum at 300 K and the optical band gap (1.28 eV) was at the minimum [23]. Polycrystalline $Cu_{1-x}Co_xFe_2O_4$ nanoparticles were synthesized using the self-igniting route, and it was reported that the lattice constant increased with the addition of Co^{2+} cations. VSM analysis suggested that the magnetic parameters increased as the concentration of Co^{2+} cation increased. Co-Cu ferrite has a maximum value of saturation magnetization (66.1 emu/g) and coercivity (960 Oe) at $x = 0.9$ [24]. $Zn_{1-x}Cu_xFe_2O_4$ was synthesized using a microwave (MW) combustion process and confirmed that the lattice constant decreased with the addition of Cu^{2+} cation. The maximum saturation magnetization (58.58 emu/g) was at $x = 0.5$. The study of UV-vis analysis at room temperature (RT) confirmed that the minimum energy band gap was 1.95 eV at $x = 0.5$ [25]. Co^{2+} doped Cu-Zn nanoparticles ($Cu_{0.7}Co_xZn_{0.3}Fe_2O_4$) were developed via the self-igniting process, and the impact of Co^{2+} on the structural, thermal, and magnetic behavior of Cu-Zn ferrites was observed. The minimum lattice constant was observed at x=0.1 and maximum saturation, $M_S = 79.63$ emu/g was at $x = 0.3$ [15].

Many researchers have studied the impact of the addition of La^{3+} into nano-ferrites. In the lanthanide series, lanthanum is the lightest and second most abundant element of rare earth (RE). At atmospheric pressure, La^{3+} is known as a superconducting RE element [26]. There had also been observed remarkable variations in the electrical, optical, dielectric, and magnetic properties by adding La^{3+} ions [6], [27-31]. Substitution of La into $ZnFe_{2-x}La_xO_4$ (x = 0, 0.02, 0.04, 0.06) nanoparticles enhanced the saturation magnetization (16.4 emu/g) and remanent magnetization (10.57 emu/g) at x=0.02. Due to the hindered crystal growth caused by the rare earth La cations into $ZnFe_{2-x}La_xO_4$, the crystallite size decreased from 37.6 to 27.4 nm, and the energy bandgap increased from 1.87 to 1.97 eV. At *x*=0.02, the observed crystalline size and band gaps were 36.9 nm and 1.89 eV, respectively [27]. La^{3+} doped Co soft ferrites with chemical formula $CoLa_xFe_{2-x}O_4$ were developed using the sol-gel route. The lattice constant decreased with the addition of La^{3+} cations, and at *x*=0.05, the minimum crystallite size (4.5 nm) was observed. The energy bandgap decreased from 1.34 eV to 1.1 eV with the addition of the dopant. VSM studies showed that the minimum saturation magnetization for $x = 0.05$ was 27 emu/g [6]. Deepapriya *et al.,* reported saturation magnetization of La^{3+} doped Cu^{2+} ferrite was 0.7288 emu/g and with crystallite size 14 nm [29].

Co-Zn nanoparticles doped with La^{3+} ($Co_{0.5}Zn_{0.5}La_xFe_{2-x}O_4$) were prepared via a sol-gel auto igniting process and studied for their structural, optical, and morphological behavior. The crystallite size was found to decrease with the addition of La^{3+} impurity, with a minimum value of 18.70 nm at $x = 0.125$. Micrograph revealed that the particle size was nanoscale and uniformly distributed for $x = 0.125$ [30]. $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ was developed via the self-propagating route, and the impact of La^{3+} on the microstructural and magnetic behavior of ferrites powder was examined. The crystallite size had a minimum value of 47.1 nm at $x = 0.07$, and lattice constant increased up to $x = 0.03$ and after $x = 0.03$ decreased. SEM analysis revealed that the mean particle size for *x*=0.01 was 132.80 nm. *M-H* curve revealed that pure Cu-Zn nano ferrites had a maximum magnetization value of 64.80 emu/g, which increased with the La^{3+} content at room temperature [31]. Cu-Co nanoparticles powder was developed via a sol-gel method with the addition of impurity La^{3+} cations with the compositional formula $Cu_{0.5}Co_{0.5}Fe_{2-x}La_xO_4$ ($0.0 \leq x \leq 0.05$ with an increment of 0.01) calcined at 1173 K. XRD results revealed that the crystallite size decreased with the substitution of La^{3+} and at $x = 0.03$ the lattice constant had a minimum value. La^{3+} doped Cu-Co nano ferrites maximum saturation magnetization was $M_S = 54.95$ emu/g and decreased with the addition of dopant [28].

This combination of outstanding properties in Zn [20], Co [21], Cu [22], Zn-Co [23], Co-Cu [24], Cu-Zn [25] and Cu-Co-Zn [15] ferrites and La^{3+} doped Zn [27], Co [6], Cu [29], Co-Zn [30], Cu-Zn [31], Cu-Co [28] ferrites, motivates for deeper analysis of nature and properties of Zn-Co-Cu ferrites in general and comprehensive analysis for the effect of La^{3+} cations doping on Zn-Co-Cu nano ferrites. To the best of our understanding and knowledge from the previous review of the literature to date, there is no literature present proposing the impact of La^{3+} on the properties of $Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{2-x}La_xO_4$ (Zn-Co-Cu) ferrites powder.

In this work, $Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{2-x}La_xO_4$ ($0.0 \leq x \leq 0.05$ with the step interval of 0.0125) nano ferrites powder was produced through the sol-gel auto combustion technique to the optimization of the structural, optical, electrical, dielectric, ferroelectric, and magnetic properties. The prepared samples were studied using different characterization techniques including XRD, SEM, UV-Vis, VSM, dielectric measurements, and two probes electrical resistivity measurements, to explore further the impact of La^{3+} doping on the properties of Zn-Co-Cu nano ferrites powder.

2 Experimental method

2.1 Materials used and synthesis method

Highly pure analytical reagent (AR) grade chemicals were used as preliminary ingredients including Lanthanum (III) [$La(NO_3)_3.6H_2O$] nitrate hexahydrate (99.99%), Zinc (II) [$Zn(NO_3)_2.6H_2O$] nitrate hexahydrate (98.0%), Cobalt (II) [$Co(NO_3)_2.6H_2O$] nitrate hexahydrate (98.5%), Copper (II) [$Cu(NO_3)_2.3H_2O$] nitrate tri-hydrate (99.99%), Iron (III) [$Fe(NO_3)_3.9H_2O$] nitrate nonahydrate (99.95%). Citric ($C_6H_8O_7$) acid was chosen as the fuel agent to synthesize Lanthanum doped Zn-Co-Cu ferrite powder. With stoichiometric calculations, the molar ratio was kept at 1:1 for metal nitrates to citric acid. The solution was placed on a magnetic stirrer with uniform stirring speed 50 rev/min. Ammonia (NH_3) solution was added to acquire a pH of 7 while maintaining a temperature of 353 K during the stirring procedure. The solution was first transformed into a gel and then burned in an auto combustion manner to transform into fluffy loose powder. The obtained powder was calcinated at 773 K for 2 h, and then sintered at 1073 K for 8 h and finally grounded to obtain a fine powder, graphic representation of the process is shown in Fig. 1.

2.2 Characterization techniques used

The structural changes of as-prepared lanthanum doped Zn-Co-Cu ferrites powder characterized via XRD (D8 Advanced, Bruker, Cu-Kα radiation, and $\lambda = 1.5418$ Å) to obtain Bragg angle (2θ) range 20^{o}-60^{o}. Phase identification and Rietveld refinement were performed with Match! Phase Identification from Powder Diffraction and FullProf software, respectively. Nova NanoSEM series 450 used for studied surface morphology, such as to investigate the particle size and shape. UV-Visible Double Beam Spectrophotometer (UV-DS) Model Lambda 25, Perkin Elmer, was taken to measure the UV-visible spectroscopy of as-prepared samples. KEITHLEY, Model 2401 Sourcemeter, Current/Resistance/Voltage Measure Meter (I-V measurement meter) used with two probes method in the present research work to measure the electrical properties. Dielectric measurements were performed by employing the IM3533 series LCR Meter and Impedance Analyzer (I-A) at room temperature (RT). Precision Ferroelectric Analyzer Testing System of Radiant technology having model No. P-PMF used to investigate ferroelectric properties.

3 Results and Discussion

The prepared $Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{2-x}La_xO_4$ ($0.0 \leq x \leq 0.05$ with the step interval of 0.0125) nano ferrite powder was characterized using various characterization techniques. The detail of characterization techniques results is explained in the following subsections:

3.1 X-ray Diffraction (XRD)

The XRD spectra for $Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{2-x}La_xO_4$ (x = 0.0, 0.0125, 0.025, 0.0375, 0.05) ferrites powder are presented in Fig. 2. Six XRD peaks were observed at $2\theta = 29.94^{o}$, 35.28^{o},37.90, 42.89^{o}, 53.24^{o} and 56.76^{o} which corresponds to (220), (311), (222), (400), (422) and (511) planes respectively, which confirm the formation of spinel structure (space group; *F d -3 m*) nano ferrites [32]. A minor peak at $2\theta = 32.18^{o}$ is also observed in the samples with x = 0.025, 0.0375, 0.05, which belongs to the secondary phase orthorhombic structure $LaFeO_3$ (space group; *P b n m*) [33, 34]. The XRD pattern represents the linear relation between the intensity of $LaFeO_3$ peak and La^{3+} concentration (x), i.e., with increasing La^{3+} ions concentration (x), the intensity of $LaFeO_3$ peak increased that confirms the low solubility of La^{3+} cations into the spinel ferrite matrix. Different crystallographic parameters were calculated using the major peak corresponding to (311) plane and are given in Table 1 and Table 2.

It is observed in Table 1 that experimental lattice constant (a_{exp}) and d-spacing (d) [35] decreased with increase in La^{3+} concentration (x) except at $x = 0.0375$. The reduction in the lattice parameters with the addition of rare earth (RE) cations is because of partial replacement of RE cations in the lattice site. During the sintering, some RE cations reside in the grain boundaries and an isolated thin layer around the grains formed. The smaller amount of RE cations getting substituted in the sublattice and larger RE cations diffuse in the grain boundaries [36]. The crystallite size 'D' was calculated via the Scherrer's equation [37, 38]. It is noted that crystallite size decreased with increasing La^{3+} concentration (x) except at $x = 0.0375$, which is in good agreement with the literature [31]. The changes in above said parameters are related due to the replacement of Fe^{3+} cations with La^{3+} cations on the octahedral (B) sites. As the cationic radius of La^{3+} cations (1.05Å) is greater than that of Fe^{3+} cations (0.645Å), it is difficult to replace the Fe^{3+} ions, which therefore disturbed the symmetry of crystal structure. Moreover, some redundant La^{3+} ions remain, which resulted in the formation of $LaFeO_3$ on the grain boundaries [39]. A considerable amount of energy is needed to substitute La^{3+} cations for Fe^{3+} cations due to greater bond length of La^{3+}_O^{2-} compared to Fe^{3+}_O^{2-}, this caused the formation of $LaFeO_3$ on the grain boundaries [40].

The dislocation line density (δ) [41] of ferrite samples was found to increase by raising the La^{3+} content and is reported in Table 1. The calculated values of X-ray density (d_X) [42, 43] are reported in Table 2, which are in good agreement with the experimental parameters. It was observed that the range of X-ray density (d_X) is 5.31±0.00266 – 5.44±0.00272 g/cm^3 and note that the molecular weight of the as-prepared samples with La^{3+} concentration (x) increases, this behavior shows that as La^{3+} concentration (x) increases, the X-ray density (d_X) increases. It can be seen that bulk density (d_B) of the samples increased with increments in La^{3+} concentrations (x), with the range of bulk density (d_B) being 4.09±0.00205 – 4.65±0.00233 g/cm^3. The porosity (P) percentage [42, 44] decreased from 22.97 % to 14.52 %, with an increase in La^{3+} concentrations (x) because of the rise in the bulk density (d_B). The A-site hopping length, 'H_A' and B-site hopping length 'H_B' are linked with the experimental lattice constant. So, the calculated value of hopping length (Table 2) show the same trend with variation in La^{3+} content as the experimental lattice constant, and similar behavior as reported by Ganure *et al.* [45].

For further analysis of X-ray diffractogram, the Rietveld refinement was performed with space group (*F d -3 m*) and the atomic position, site occupancy, and profile R-factors were determined. Rietveld refined diffractograms with the difference in intensities of both observed and calculated are shown in Fig.3. Various R-factors including the weighted R-profile (R_{wp}), R-expected (R_{exp}), and goodness-of-fit ($\chi^2 = R_{wp} / R_{exp}$) were used to check the structural reliability [46, 47]. The obtained parameters from Rietveld refinement are reported in Table 3. The smaller value of goodness-of-fit (χ^2) indicated the development of the required crystalline phase. The refinements were performed until the value of "χ^2" reached close to 2 [48].

Niyaifar *et al.* [49] proposed the occupancy of Zn^{2+} only into the tetrahedral (A-) sites. The occupancy of Fe^{3+}, Cu^{2+}, and Co^{2+} cations into the A-site and B-site [24, 50]. But RE ions occupy only the octahedral (B-) site. Hence, the occupancy of La^{3+} ions only on the octahedral (B-) sites [51].

The cation distribution of as-prepared series was carried out using the intensity ratio of XRD peaks through Rietveld refinement. The atomic position ($x = y = z$) and site occupancy (g) are listed in Table 4. The estimated uniform cations distribution of the present series, as shown in Table 5.

The investigated average value of cations radii r_A and r_B at the A-site and B-site are depicted in Table 6. The calculated values of r_A remain the same but r_B increased by increasing La^{3+} concentration (x), which confirmed that La^{3+} cations occupied the octahedral site. The value of the theoretical lattice constant [52, 53] are listed in Table 6 and revealed that by raising the of La^{3+} cations, the theoretical lattice constant increased. By comparing the values, it was found there is a difference between the experimental and theoretical lattice constants, this difference is because at high concentration, there is less solubility of La^{3+} ions, and the $LaFeO_3$ compound formed. The oxygen position parameter (U) for spinel structure ferrites has an ideal value of 0.375. The estimated value of 'U' showed a small deviation from the ideal value, and decreased with dopant concentration, as indicated in Table 6, which confirmed the deformation present in the lattice structure. Ideally, the value of tolerance factor (T) has a value close to one (unity) for spinel structure ferrites. The calculated value of 'T' decreased with increasing the La^{3+} concentrations (x), listed in Table 6, but are close to one (unity), suggesting that there are no defects present in the as-synthesized samples [52].

At tetrahedral (A-) site the bond length (R_A) and at octahedral (B-) site the smallest bond length (R_B) were calculated [54]. The bond length R_A and R_B were depicted in Table 6. The magnetic interactions like (A-A) interactions, (B-B) interactions, and (A-B) interactions in spinel ferrites depend on the bond length between cation-cation and cation-anion bonds. The shared tetrahedral site edge length (R), shared octahedral site edge length (R') and unshared octahedral site edge length (R'') were determined [55]. The investigated values of R, R' and R'' were given in Table 6, which shows the variation in these parameters depends upon the La^{3+} concentration (x) and experimental lattice parameters, and change in these parameters is according to the changes that occurred in experimental lattice parameters.

3.2 Surface Morphological analysis

The scanning electron microscope (SEM) images of $Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{2-x}La_xO_4$ (x = 0.0, 0.0125, 0.025, 0.0375, 0.05) ferrites samples at a magnification of 100000 × (500 nm scale) are depicted in Fig. 4 (a-e). The microstructure images of the ferrite samples show an angular (irregular) particle size and shape. Moreover, the irregularity in size and shape of particles increases, and particle distribution uniformity and porosity decrease with La^{3+} concentration, and due to the self-igniting route, homogenous particle distribution of nano ferrite samples was achieved.

The particle sizes are between 474.1 nm to 1022.1 nm and have a maximum value at x=0.0375, as denoted in Fig. 12. It was found that the high calcination temperature leads to the agglomeration of particles because of different emerging forces such as weak Van der Waals, electrostatic and capillary forces that produce magnetic interactions among the particles [56]. It was found that agglomeration increased with La^{3+} concentrations (x). The micrograph of the undoped as-prepared sample (Fig. 4 (a)) indicates the existence of the monophasic spinel microstructure. In contrast, the addition of La^{3+} ions (Fig. 4 (b-e)) shows a multiphasic spinel microstructure having a larger matrix of ferrites particles and at the grain boundaries a smaller $LaFeO_3$ secondary phase [57, 58].

3.3 Ultraviolet-Visible (UV-vis) Spectroscopy Analysis

The optical band gap of materials generally depends upon grain size, the concentration of dopant element, lattice structure parameters, lattice strain, surficial impact, and presence of impurities [59]. UV-vis spectroscopy was employed to determine the optical band gaps for samples due to the first and second absorption band. Tauc plots of the as-prepared ferrites are depicted in Fig. 5. It observed from the data that the first optical band gap (E_g) of the ferrite samples due to the first absorption band lie in the range of 1.94±0.0097 to 2.49±0.0124 eV and have a minimum value at x = 0.0375, due to the electrons at low energy being inactive (Fig. 5). On the other hand, high energy electrons are active at the second optical band gap (E_g') due to the second absorption band having a maximum value at x = 0.0375. The optical bad gap lies in the range 5.54±0.00166 to 5.62±0.00169 eV (Fig. 5). These energy gaps from the 1st and 2nd band may be due to the ferro and para nature of materials, respectively.

3.4 I-V Measurement Analysis

Measurements of current-voltage (I-V) were carried out on pellets via two probes method to investigate the electrical properties of $Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{2-x}La_xO_4$ (x = 0.0, 0.0125, 0.025, 0.0375, 0.05). The samples were placed one by one in the sample holder, then connected to the two electrodes of the furnace. The required temperatures were maintained using a temperature controller. The DC resistivity of the samples was determined at temperatures from 303 K to 673 K with a step of 10K.

It is noted from Fig. 6 that the transition temperature after which the DC resistivity of the material change is known as the Curie temperature. The region below Curie temperature is called the ferromagnetic region. The region above the Curie temperature is a paramagnetic region. The impact of temperature (T) on the log of DC resistivity ($log\ \rho$) of La^{3+} doped Zn-Co-Cu nano ferrite, is seen in Fig. 6. From Fig. 6, it is clear that DC resistivity decreased with an increasing La^{3+} concentration and has a minimum value at $x = 0.0375$ in both ferromagnetic and paramagnetic regions.

Different conducting channels such as Fe^{3+}–Me (Me is Zn^{2+}, Co^{2+}, $Cu^{2+,}$ and La^{3+}) and Fe^{3+}–Fe^{3+} are responsible for the charge hopping in the as-prepared nano ferrites. Partial replacement of Fe^{3+} via rare earth (RE) cations induced lattice distortion and strain in the spinel matrix modified the electrical properties [60]. La^{3+} cations have a strong octahedral (B-) site preference. Therefore, by adding the La^{3+} cations, Fe^{3+} cations replaced by La^{3+} cations at the octahedral (B-) site limits the conductivity.

The Arrhenius plots ($log\ \rho$ vs $1000/T$) for La^{3+} doped Zn-Co-Cu nano ferrite are shown in Fig. 7. The activation energy (ΔE) was determined by taking the slope of Arrhenius plots [61]. It is noted from Fig. 7 that the transition temperature after which DC resistivity (ρ) decreased referred to as the Curie temperature (T_C). The Curie temperature (T_C) creates magnetic disorder in the nano ferrites. It was clear from VSM analysis saturation magnetization present in all the samples at RT (Fig. 11). Therefore, the as-prepared samples are ferromagnetic. It was observed that with an increasing Curie temperature, the saturation magnetization decreased, and resistivity increased up to Curie temperature. So, after Curie temperature (T_C), all the samples became ferromagnetic. According to the magnetic theory of semiconductors, the activation energy of the paramagnetic region must be greater than the ferromagnetic region. The magnetic order exists in a ferromagnetic state and magnetic disorder in the paramagnetic state, as reported by Raghasudha [61]. The electric charge carriers, therefore, require less energy in the ferrimagnetic state compared to the paramagnetic state for the conducting process. It also shows that the conduction in nano ferrites is affected by the magnetic disorder, as proposed by Lakhani and Modi [62]. The determined values of the "ΔE" of the ferrite samples are shown in Fig. 8. It was found that "ΔE" lies between the range 1.2064±0.0036 to 1.3702±0.0041 eV and has a minimum value at $x = 0.0375$. It was found that DC resistivity (ρ) and the activation energy (ΔE) both have a minimum value at $x = 0.0375$, as seen in Fig. 8. The calculated value of the Curie temperature (T_C) from "1000/T" vs. "$log\ \rho$" curves are reported in Fig. 7. It can be seen that the Curie temperature (T_C) has a maximum of 370 K at $x = 0.0375$. The drift mobility (μ_d) of the samples were determined [63] and the value at RT is $0.3682 \pm 0.0018 \times 10^{-30}$ cm^2/Vs, $0.4118 \pm 0.0021 \times 10^{-30}$ cm^2/Vs, $23.8342 \pm 0.1192 \times 10^{-30}$ cm^2/Vs, $29.9584 \pm 0.1498 \times 10^{-30}$ cm^2/Vs and $0.5100 \pm 0.0026 \times 10^{-30}$ cm^2/Vs respectively. It can be seen at RT, the drift mobility (μ_d) has a maximum value, and DC resistivity has a minimum value at x=0.0375. It was found that the as-prepared sample has a greater value of DC resistivity (ρ) with a smaller value of drift mobility (μ_d) and vice versa [64]. The UV-vis analysis of $Zn_{0.5}Co_{0.025}Cu_{0.025}Fe_{2-x}La_xO_4$ ($0.0 \leq x \leq 0.05$ with the step interval of 0.0125) demonstrated that the first optical energy bandgap (E_g), DC electrical resistivity (ρ) and activation energy have a minimum value at $x = 0.0375$ as reported in Fig. 8.

3.4 Dielectric Analysis

To measure the dielectric properties of La^{3+} doped Zn-Co-Cu ferrite samples, an LCR meter, was used. Lodhi *et al.* [65] proposed that the dielectric properties depended upon different parameters like the method of preparation, stoichiometric calculation, grain size, sintering temperature, Fe^{3+}/Fe^{2+} ratio, cation distribution, and oxygen parameters. All of this is normal behavior of soft nano ferrites, due to a lagging at different lattice sites of hopping electrons existing between Fe^{3+} and Fe^{2+} ions. Moreover, as the frequency increases, Fe^{2+} ions are responsible for different types of polarization behind the electric field, which form at high temperatures during sintering, as proposed by Raghasudha *et al.* [66]. Koop′s theory described that all kinds of polarization exist at low frequency. Still, because of space charge growth at the grain-grain interface, interfacial polarization is more prominent, and accumulated charges act as a barrier for hopping electrons. Due to the barrier, the voltage drops at the grain interface, and a very thin layer of spatial charge carriers form at the grain interface. The grain boundary impact is more prominent at low frequency, as reported by Gul and Maqsood [67].

At low frequency, the grain boundaries show the large value of dielectric tangent loss because the thickness of the barrier layer and capacitance have inverse relation, i.e., $C \propto \frac{1}{d}$. Debye relaxation appeared in all the samples except $x = 0$ and increased towards low frequency and high frequency with a concentration of La^{3+}. It is dominant throughout the whole frequency range. At high frequency, interfacial polarization in the materials shows that dielectric constant and loss is zero. Still, Debye type relaxation exhibits nonzero dielectric constant and loss at high frequency. It was found that at high frequency, the dielectric tangent loss has a nonzero value, which confirms that Debye type relaxation exists and is consistent with the literature [68]. Dipolar materials have Debye relaxation due to orientational polarization, and this polarization occurs due to dipole's rotational displacement. The rotational displacement also increases with La^{3+} cations concentration (x) because the La^{3+} cations radii are greater than the Fe^{3+} cations radii, as reported in the XRD analysis. The frequency of the charge carrier transfer at high frequency cannot follow the external electric field, and this results in a decrease in the dielectric loss, as described by Roy and Bera [57]. An increase in the La^{3+} cation concentrations, means the polarizability of La^{3+} doped Zn-Co-Cu nano ferrites decreased. Hence, Debye type orientational polarization increased individually.

The dielectric tangent loss ($tan\delta$) defined as the ratio between the dielectric loss to a dielectric constant, which measured the loss of electrical energy by an external electric field applied to as-prepared samples at different frequencies for all the concentration was determined [69]. Fig. 9 represents the variation between dielectric tangent loss ($tan\delta$) and log of frequency ($log\, f$) for as-prepared nanoferrites for the frequency range 8 Hz to 8 MHz. The $tan\delta$ decreased with the frequency at RT and had a high value at low frequency because of the very thin barrier layers, which are more prominent than the conducting grains, which caused the higher value of the dielectric tangent loss. It can be seen from Fig. 9 dielectric loss has a minimum value at x=0.0375.

3.5 Ferroelectric Analysis

Spontaneous electric polarization exists in some crystalline materials that can be made switchable by an applied external field; such materials are known as ferroelectric and are the electric analog of ferromagnets. A Radiant technology precision ferroelectric analyzer testing system was used to investigate the polarization in the $Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{2-x}La_xO_4$ ($0.0 \leq x \leq 0.05$ with the step interval of 0.0125) samples. The ferrite powder was pressed into disk shape pallets for the analysis. By applying an ac voltage, a corresponding electric field (E) was produced, causing electric polarization (P) in the samples and a hysteresis loop formed known as P-E

hysteresis loop, or simple *P-E* loop was recorded [70, 71]. Fig. 10 shows the *P-E* loop for nano ferrite samples. Routray *et al.* [72] proposed that orientations of domains, defects, composition, electric field, and homogeneity are factors upon which polarization properties depend. A banana shape *P-E* loop was found in all the samples [73].

The *P-E* loop formation is symmetrical around the origin, demonstrating that the electric dipoles are distributed uniformly inside the materials. By increasing the applied field, a regular increase in the maximum polarization (P_m) and remnant polarization (P_r) were observed, which is a clear indication that the relevant series belongs to linear dielectrics, as described by Samad *et al.* [74]. A banana-shaped trend attributed to high eddy current or dielectric losses and oxygen vacancies were formed on the top surface grains, resulting in leakage current [75]. But as a whole behavior, the *P-E* loops showed the ferroelectric nature of the as-prepared samples were reduced with the addition of La^{3+} cations, similar behavior was proposed by Naresh *et al.* [70].

3.6 VSM Analysis

The *M-H* loops of the $Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{2-x}La_xO_4$ ($0.0 \leq x \leq 0.05$ with the step interval of 0.0125) ferrites powder at RT were recorded using a VSM (Fig. 11). From Fig. 11, it is clear that the *M-H* loops of the as-synthesized samples have a small area (narrow loop). Hence the as-prepared samples exhibit soft nature magnetic material [76]. The magnetization saturation (M_S), remanence (M_r), coercivity field (H_C), anisotropy constant (K) and experimental magnetic moment (n_B^e) were determined from the *M-H* loop of each sample and given in Table 7. It can be seen that M_S, M_r, H_C, n_B^e and K decreased with dopant La^{3+} ions except at $x = 0.0375$, where these parameters have the highest value as compared to the other prepared samples due to the higher crystallinity and uniform morphologies. The substitution of paramagnetic La^{3+} cations results in the development of the non-magnetic spinel structure. The theoretical magnetic moment (n_B^t) was calculated by the difference of the magnetic moment of trihedral (*A*-) and octahedral (*B*-) sites ($n_B^t = M_B - M_A$) [77]. The magnetic moments for $Zn^{2+}(0\mu_B)$, $Co^{2+}(3\mu_B)$, $Cu^{2+}(1\mu_B)$, $Fe^{3+}(5\mu_B)$ [78] and $La^{3+}(0\mu_B)$ [79]. For La^{3+} doped Zn-Co-Cu nano ferrites, $La^{3+}(0\mu_B)$ replaced $Fe^{3+}(5\mu_B)$ cations at *B* sublattice, which leads to a decrease in the octahedral sublattice magnetization (M_B). Moreover, tetrahedral sublattice magnetization (M_A) remain the same as cations distribution remain the same at *A*- site (as shown in Table 5), which leads to a decrease in the net magnetic moment (n_B^t). The experimental and theoretical magnetic moment (n_B^e and n_B^t) is reported in Table 7. It can be seen from Table 7 that the theoretical magnetic moment (n_B^t) decreased with La^{3+}

concentration and the experimental magnetic moment (n_B^e) also decreased except $x = 0.0375$. The decreasing behavior of magnetization and magnetic moment is owing to the nonzero Yafet-Kittel (Y-K) angle [77]. The nonzero spin canting (Y-K angles) angles suggest that the magnetic behavior cannot be described on the base of Neel two sublattice model because of the existence of the non-collinear spin matrix on the octahedral (B-) sublattice. Therefore, the A-B interaction was decreased and the B-B interaction was increased. Furthermore, Y-K angles can be determined using $n_B^e = M_B \cos\cos\alpha_{y-k} - M_A$ (Table 7) [19]. The spin canting angles of the as-prepared series of samples increased with La^{3+} concentration suggest that the increased favor for triangular spin arrangement on octahedral (B-) sublattice and A-B interaction decreased. The substitution of dopant ions caused the change of the collinear ferromagnetic order into non-collinear disintegration and arrangement of ferromagnetic order that decreased the value of M_S [80]. The "*D*" was a minimum for x = 0.0375 (Table 1) and the magnetization saturation (M_S) had it's the highest value for $x = 0.0375$. For $x > 0.0375$, the crystallite size (D) increased with decrease in magnetization saturation (M_S) indicating a superparamagnetic behavior. Because $Zn_{0.5}Co_{0.25}Cu_{0.25}Fe_{1.95}La_{0.05}O_4$ has the impurity $LaFeO_3$ residing in the grain boundaries, this causes internal stress, which affects the saturation magnetization magnitude [81].

It can be seen from Fig. 12 that the saturation magnetization (M_s) and the particle size of the as-prepared ferrite samples decreased up to x=0.025, with both having maximum values at x=0.0375. On the other hand, the magnetic moment also depends on particle size, and at x=0.0375, the particle size and number of aligned magnetic moments increased. Hence, saturation magnetization (M_S) is increased. It can also be seen from Fig. 12 that the decrease in Curie temperature (T_C) with an increase in La^{3+} concentration up to $x = 0.0125$ also confirmed that the disorder of magnetic moments exists.

The performance of microwave absorbing devices is affected by electric or magnetic losses. Therefore, a microwave frequency (ω_m) is considered as an operating frequency for the performance of the microwave absorbing devices prepared from nano ferrites. The microwave frequency (ω_m) was calculated using $\omega_m = 8\pi^2\gamma M_S$, where $\gamma = 2.8$ MHz/Oe is the gyromagnetic ratio [82]. Akhtar *et al.* prepared Co^{2+} doped Mg-Zn nano ferrites and reported microwave frequency (ω_m) range for all the samples was 2.84 to 5.96 GHz [83]. The high resistivity and low losses ferrites are applicable to microwave devices [71].The calculated values of operating microwave frequency (ω_m) for sample $x = 0.0125$ lies in the range of 6 to 7 GHz, as shown in Fig. 13 and best for C-band microwave frequency applications. On the other hand, it is clear from Fig. 13 that sample x=0.0375 has an operating microwave frequency (ω_m) range 8 to 12 GHz, which is applicable for X-band microwave frequency applications.

4 Conclusion

In this study, lanthanum doped Zn-Co-Cu soft ferrite powder were synthesized via the self-igniting route. It was observed that the experimental lattice constant decreased except at $x = 0.0375$ because of the larger radii of La^{3+} cations. It also found that crystallite size decreased except at $x = 0.0375$ and range of X-ray density (d_X) was 5.31 ± 0.00266 to 5.44 ± 0.00272 g/cm^3. Besides, the micrograph investigation shows the non-uniform size and shape of ferrite samples. UV-vis results revealed that more than one optical energy band gaps exist in the as-prepared samples, which is consistent with DC electrical resistivity at RT. LCR studies gave information about the dielectric behavior of the samples, and the values of energy loss decreased with an increasing frequency. La-doped Zn-Co-Cu samples showed a ferroelectric nature confirmed by the *P-E* loops. *M-H* loops indicated that "M_S" has a maximum value at $x = 0.0375$. The microwave frequency response for La-doped Zn-Co-Cu ferrite samples x=0.0125 and x=0.0375 in the microwave frequency range region determined using the magnetization (M_S). The calculated values of operating microwave frequency (ω_m) for $x = 0.0375$ lies in the range of 8 to 12 GHz, which would be applicable for X-band microwave frequency applications.

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