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Lanthanum doped $Zn_{0.5}Co_{0.5}La_xFe_{2-x}O_4$ spinel ferrites synthesized *via* co-precipitation route to evaluate structural, vibrational, electrical, optical, dielectric, and thermoelectric properties

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Abstract

Lanthanum doped $Zn_{0.5}Co_{0.5}La_xFe_{2-x}O_4$ spinel ferrites were synthesized *via* the co-precipitation technique. To characterize the structural, vibrational, electro-optical, dielectric, and thermoelectric properties, the following characterization techniques X-ray diffraction (XRD), Fourier transformation infrared (FTIR) and Raman spectroscopy, I-V measurement analysis, UV-vis spectroscopy, LCR meter, Seebeck analysis, and Energy dispersive X-ray analysis (EDX) were used. The XRD patterns showed nano-crystalline single-phase structure formation. Moreover, the lattice constant increased from $8.3909 \pm 0.0042 \text{ \AA}$ to $8.3994 \pm 0.0042 \text{ \AA}$, and the crystallite size reduced from 33.6 to 17.5 nm with increasing La^{3+} cations. The bond angles showed stronger $A-A$ and $A-B$ interactions and weak $B-B$ interactions with the addition of La^{3+} . FTIR spectra showed the existence of the M-O stretching band and functional group study. The resistivity, optical band gap, and activation energy had maximum values at $x = 0.1$. At room temperature (RT), the dielectric parameters were recorded between the range of 8 Hz to 8 MHz. The Seebeck voltage coefficient was obtained for the as-prepared nano-ferrites to determine the charge carrier type. The EDX spectra showed a compositional distribution of the elements in all the samples.

Keywords: co-precipitation method; structural; electro-optical; dielectric;

1 Introduction

The nano-level methodology initiated by Professor Feynman has witnessed drastic changes in the understanding of materials research over several decades [1]. Magnetic nanomaterials have a prominent place in established material science because of their importance in various technological areas [2, 3]. Numerous magnetic materials have demonstrated their versatility in a variety of applications, from heat transport fluid to inductive heat production [4, 5], from magnetic data recorders to microwave devices [6-8], and from medical diagnostics to disease treatments [9-11]. Nano ferrites are a primary material within the category of magnetic materials consisting of mixed composition of transition metal cations and iron oxide. Nano ferrites are divided into three main areas based on their crystal matrix, i.e., hexagonal, spinel, and garnet nano ferrites. Spinel ferrites are the most promising of these three types of ferrites because of their stable and straightforward lattice structure, versatile cation distribution, suitable properties, easy preparation, and accommodation of dopant ions [12-18]. The cation distribution between the two-spinel ferrite intrinsic lattice sites is subjected to ions balance. Typically, the metal ions prefer site energies that characterize normal spinel or inverse spinel or mixed spinel matrix behaviour [19]. The different properties of spinel ferrites are improved by various means such as stoichiometric proportions, preparation method, inclusion of metal divalent or trivalent cations in the spinel lattice, etc. The methods of preparation often affect the shape and the crystallite size of nano ferrites, resulting in structural change [17, 18]. The integration of dopant ions into a lattice, either divalent/trivalent or magnetic/nonmagnetic, results in a drastic change in structural and other properties by cations distribution. In this context, the selection of dopants is a prerequisite for achieving the desired improvement in the pristine spinel ferrites. In addition to transitional dopants like Zn^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , rare earth metals cation dopants like La^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Eu^{3+} , Ho^{3+} , Gd^{3+} , etc can be added in small amounts, resulting in a radical change in the spinel ferrites [20, 21].

Several researchers studied La^{3+} doped Zn [22], and Co [23, 24] nano ferrites. Bahhar *et al.* examined the impact of La^{3+} on various properties of Zn nano ferrites and described that crystallite size obtained from XRD analysis decreased with La^{3+} concentration [22]. Hemeda *et al.* synthesized $CoLa_xFe_{2-x}O_4$ by employing the ceramic route and claimed that the secondary phase of $LaFeO_3$ formed as a concentration of La^{3+} increased, and resistivity decreased as the dopant concentration increased. This decreasing trend in resistivity suggests that the conduction process for as-prepared samples is due to the hopping of charge carriers

[23]. $CoLa_xFe_{2-x}O_4$ was developed using the co-precipitation technique. The impact of La^{3+} on electrical and dielectric parameters of Co^{2+} ferrites were investigated. The dielectric loss decreased with La^{3+} concentration, and at $x = 0.2$ had a minimum value. The DC electrical resistivity of pure cobalt ferrites was $6.465 \times 10^5 \Omega \text{ cm}$ and increased with the dopant content [24].

There are many goal-oriented methods of preparation, like the microemulsion process [25], self-igniting auto combustion route [26, 27], co-precipitation method [28-30], and the hydrothermal method [31]. There is no literature at present on the La^{3+} doped Co-Zn spinel ferrite samples produced using the co-precipitation method. The co-precipitation method was used due to the high yield, not requiring the use of organic solvents, high product purity, and ease of reproducibility. It is also easier, more convenient to control the particle size and a low-cost route of preparation [32-34]. The aim of our work is the optimization of the structural, vibrational, electro-optical, dielectric, and thermoelectric properties in $Zn_{0.5}Co_{0.5}La_xFe_{2-x}O_4$ ($0.0 \leq x \leq 0.1$ with a step interval of 0.025) spinel ferrite samples at low sintering temperature prepared by the co-precipitation route.

Mugutkar *et al.* synthesized Zn-Co (ZC) nano ferrites with the substitution of Gd^{3+} and reported lattice impactions and strain were enhanced in the crystals [35]. The crystalline size (D) increased with the substitution of Nd^{3+} in Zn-Co ferrites [36]. Almessiere *et al.* reported that pure Zn-Co ferrite has a maximum value optical bandgap, which increased with the addition of Nd^{3+} cations [37]. The activation energy and electrical resistivity were enhanced *via* substitution of Pr^{3+} in Zn-Co nano ferrites [38]. The changed in the Raman modes confirm the destruction in lattice matrix in Ho^{3+} doped ZC ferrites and optical bandgap was increased with the addition of dopant [39]. Hence, as compared to other rare-earth doped ZC nano ferrites La^{3+} substituted Zn-Co ferrites have a small crystalline size and high electrical resistivity.

2 Experimental detail

2.1 Material and Method

$Zn_{0.5}Co_{0.5}La_xFe_{2-x}O_4$ ($0.0 \leq x \leq 0.1$ with a step interval of 0.025) powder was prepared using a co-precipitation route. For this purpose, highly pure AR grade chemicals Co $(NO_3)_2 \cdot 6H_2O$ (98.5%), La $(NO_3)_3 \cdot 6H_2O$ (99.99%), Zn $(NO_3)_2 \cdot 6H_2O$ (98%), and Fe $(NO_3)_3 \cdot 9H_2O$ (99.95%), were used according to stoichiometry calculations. The precursors of the series were mixed in de-ionized water to achieve a solution of 100 ml for each nitrate separately, which was then put in the magnetic stirrer at $80^\circ C$. Sodium hydroxide was added

drop by drop in this solution to achieve pH 12. The hydroxides of the metals used were produced at this pH value and the size of the particles and their nucleation rate were also controlled. To obtain precipitates, ferrite samples were placed in the preheated water bath at 80°C for 12 hours. These precipitates were collected using filter paper and dehydrated in the oven at 80°C for 24 hours. Then the as-prepared samples were ground in the ceramic mortar to obtain fine powder. The as-prepared samples were then sintered at 1023 K in a muffle furnace, and characterized by different techniques. The schematic step by step version of the co-precipitation route is represented in Fig. 1.

2.2 Characterization Techniques Used

To record the diffraction peaks, the X-ray diffractometer (Bruker D8 Advance) with $\lambda = 0.154$ nm and a 2θ range of $20^\circ - 60^\circ$ was used. FTIR spectroscopy (Perkin) was employed to confirm absorption band spectra within the range of wave number 3000 to 400 cm^{-1} . Raman spectra were recorded using the LABRAM-HR commercial spectrometer. The DC resistivity was determined by the I-V measurement technique (Keithley Electrometer Model 2400). UV-Visible Double Beam Spectrophotometer (UV-DS) Model Lambda 25, Perkin Elmer was used to measure the energy bandgap (E_g). IM3533 series LCR Meter used for the dielectric measurements. The thermoelectric properties were measured as a function of temperature for all the samples by a Keithley Electrometer.

3 Results and Discussion

3.1 Structural Analysis

Diffraction investigations were performed using X-rays, to confirm the phase developments and crystallinity of $Zn_{0.5}Co_{0.5}La_xFe_{2-x}O_4$ (where $x = 0.0, 0.025, 0.05, 0.075, 0.1$ and 0.125) nano ferrite powder. X-ray diffractogram for La^{3+} doped Zn-Co (La^{3+} doped ZC) nano ferrite samples fabricated *via* the co-precipitation route are depicted in Fig. 2, after sintering at 1023 K.

The diffraction peak positions appeared at $30.03^\circ, 35.40^\circ, 37.02^\circ, 42.96^\circ, 53.35^\circ,$ and 56.87° , which concur with (220), (311), (222), (400), (422), and (511) planes respectively of La^{3+} doped ZC (JCPDS#77-0013). Thus all the samples, were FCC (Face centered cubic) single-phase spinel structures belonging to the space group; $Fd-3m$ [27, 40]. No extra peaks related to La^{3+} or byproducts were observed for samples $x = 0.0$ to 0.075 . But at a higher concentration of La^{3+} , very small intensity peaks were observed between the two peaks (222) and (400), and another peak was found between the peaks (422) and (511) for the samples $x = 0.1$ and $x = 0.125$ corresponds to $LaFeO_3$ (JCPDS#75-0541). The highest intensity peak (311)

was used to calculate the values of the different lattice parameters. The calculated values of the crystallite size (D) [41] are given in Table 1. It can be seen that the values of “ D ” for all the prepared samples decreased from 33.6 to 17.5 nm, with increasing La^{3+} doping. This may be because of the difference in ionic radii between La^{3+} (1.06 Å) and Fe^{3+} (0.67 Å) cations, This decrease in crystallite size is due to the bond formation energy of $\text{La}^{3+}\text{-O}^{2-}$ and $\text{Fe}^{3+}\text{-O}^{2-}$, since the bond energy of La-O is greater than Fe-O which signpost that the more energy is required for the replacement of La^{3+} at the octahedral site in Zn-Co nano ferrite. Due to this substitute La^{3+} cations enter at interstitial site which suppresses the crystallization of Zn-Co ferrites. [42, 43]. So, it is more difficult to substitute La^{3+} cations as compared to Fe^{3+} cations on the spinel matrix. The value of the experimental lattice constant (a_{exp}) [44] for the (311) plane is reported in Table 1. The experimental lattice constant (a_{exp}) increased linearly with the raising La^{3+} doping for the as-prepared samples, which is because of the variation between the ionic radii of both La^{3+} cations and Fe^{3+} cations. The small variation in the lattice constant is due to the replacement of La^{3+} (1.06 Å) greater cationic radii ions than Fe^{3+} (0.67 Å) ions at the octahedral site. Consequently, a small extension was observed in Zn-Co nano ferrites. The dislocation line density (δ) increased with decreasing the crystallite size (D) [45]. The dislocation line density (δ) of the nano ferrite samples increased from 8.86×10^{-4} to $31.8 \times 10^{-4} \text{ nm}^{-2}$ with increasing the La^{3+} concentration. The volume of the unit cell increased linearly from 590.78 Å^3 to 592.58 Å^3 as the La^{3+} concentration increased from $x = 0.0$ to 0.125 . Tetrahedral (A -) site hopping length H_A and octahedral (B -) site hopping length H_B were calculated [46]. It is observed from Table 1 that the magnetic ions distance increased with La^{3+} doping. This behaviour of A - site hopping length “ H_A ” and B - site hopping length “ H_B ” is analogous with the behaviour of experimental lattice constant (a_{exp}). It may be due to the difference in ionic radii of constituent cations [47].

The X-ray density (ρ_x) increased from 5.34 ± 0.00535 to $5.56 \pm 0.00557 \text{ g/cm}^3$ with the addition of the La^{3+} content (Table 2), as the increase in molecular weight overtakes, the increase in the volume of unit cell [48]. The bulk density (ρ_B) increased from 3.29 to 4.95 g/cm^3 with the addition of La^{3+} cations (Table 2). The relative density (ρ_R) decreased from 162.57 % to 112.43 % as La^{3+} doping increased from $x = 0.0$ to $x = 0.125$. The values of porosity (P) percentage for the nano ferrite powder decreased from 38.38 % to 11.05 %, with increasing La^{3+} concentrations from $x = 0.0$ to 0.125 (Table 2). The variation among the X-ray density (ρ_x), bulk density (ρ_B), relative density (ρ_R) and porosity percentage versus dopant La^{3+} are shown in Fig. 3(a). Both densities were observed to increase with increment of La^{3+} cations.

This increase in densities may be due to different ionic radii of La^{3+} (1.05 Å) as that of Fe^{3+} (0.645 Å) ions, while the porosity decreased with the addition of La^{3+} .

The packing factor (p) [49], strain (ϵ) [50], and specific surface area (S) [47] of all the samples were calculated. It was observed in Table 2 the packing factor (p) decreased with La^{3+} concentration. This may be due to the difference in the cationic radii of rare earth La^{3+} and Fe^{3+} cations [51]. The strain value (ϵ) increased with dopant concentration increase. The specific surface area (S) was also enhanced with the addition of La^{3+} cations. The variation of strain (ϵ), packing factor (p), and specific surface area (S) with La^{3+} concentrations are given in Fig. 3(b). Because of the formation of polaron (electron-phonon interactions), the charge carriers are not free in spinel ferrites but are highly localized in their d-shells. A slight polaron defect is produced as a result of the displacement of neighboring atoms or ions when a charge carrier is trapped at a given lattice site [52]. It can be noted from Table 2 that the calculated polaron radius (γ_p) increased with La^{3+} doping. This suggests that the electric charge carriers required more energy from one cationic lattice site to another. The high activation energy values calculated from electrical measurements also endorse the increase in polaron radius [52]. The plot of polaron radius (γ_p), hopping length H_A and H_B versus La^{3+} concentrations are shown in Fig. 3(c).

Several researchers have used this method to determine the cation distribution [53-55]. The La^{3+} substituted Zn-Co nano ferrites formula proposed for all the samples can be represented as $(\text{Zn}_{0.5}^{2+}\text{Co}_{0.05}^{2+}\text{Fe}_{0.45}^{3+}) [\text{Co}_{0.45}^{2+}\text{Fe}_{1.55-x}^{3+}\text{La}_x^{3+}] \text{O}_4^{2-}$. This formula is based on hypotheses; i) The sum cationic distribution at tetrahedral site is one and at octahedral site is two. ii) The spinel ferrite net charge must be zero. Therefore, to create an electrically neutral structure, the number of positive charges must equal the number of negative charges in the compound. There are eight A - sites and 16 B - sites occupied by the divalent and trivalent cations in the spinel matrix. The Zn^{2+} cations occupy A -sites rather than B -sites [51]. Co^{2+} and Fe^{3+} occupy both A - and B - sites [56]. La^{3+} cations replace Fe^{3+} cations from B -site [51].

In addition to the experimentally observed values of the lattice parameters, the average cations radius r_A at A - site, and r_B at B - site were determined [57]. It is clear from Table 3 and Fig. 4 that r_A remains the same, but r_B increased with a dopant concentration. This variation in r_B is due to the extension of B -site on substitution with greater radii La^{3+} (1.06 Å) cations [51]. The values of the theoretical lattice constant (a_{th}) increase with increasing La^{3+} (Table 3). The difference between the a_{th} and a_{exp} values is due to the approximation used for the a_{th} measurements that consider an ideal unit cell of spinel structure with cations and anions as rigid

spheres arranged regularly [58]. The variation of La^{3+} concentration versus crystallite size (D), experimental (a_{exp}), and theoretical (a_{th}) lattice constant are given in Fig. 5. The oxygen position parameter (U) was calculated using the theoretical and experimental parameters [58]. It is clear from Table 3 and Fig. 6 that the values of “ U ” decreased with dopant concentration. It is noted that the calculated values of “ U ” are higher than an ideal value ($U_{\text{ideal}} = 0.375\text{\AA}$), which is for a perfect closed packing structure, but actually, the lattice is slightly deformed, due to small movements of anions towards tetrahedral (A -) sites [59]. For a perfectly closed packed structure, the tolerance factor values (T) is one [60]. It can be observed from Table 3 and Fig. 6 that the calculated values of “ T ” decreased with an increasing La^{3+} concentration from $x = 0.0$ to $x = 0.125$. The metal-oxygen bond length “ R_A ” on A - site, and metal-oxygen bond length “ R_B ” on B - site both depend on oxygen position parameters and experimental lattice constant [61]. The calculated values of R_A and R_B are reported in Table 3. It can be seen from Fig. 4 that R_A decreased and R_B increased with La^{3+} doping. The calculated values shared tetrahedral site edge length (R_x), shared octahedral site edge length (R_x'), and unshared octahedral site edge length (R_x'') [51] are listed in Table 3 and vary in accordance with the lattice parameter.

Magnetic interaction strength plays a vital role and can be measured from the angle and distance between the ions [49]. The interionic distance between the ions, i.e., cation-anion ($\text{Me} - \text{O}$) distance (p , q , r , and s) and cation-cation ($\text{Me} - \text{Me}$) distance (b , c , d , e , and f) were calculated [49]. The calculated values of the interionic distance between the ions are in Table 4 and depicted in Fig. 7. It was found that these values depend on the La^{3+} concentration and were used to find the bond angles values θ_1 , θ_2 , θ_3 , θ_4 , and θ_5 [49]. The determined bond angles are listed in Table 5 and depicted in Fig. 9 and with La^{3+} doping, increase in values of θ_1 , θ_2 , and θ_5 indicate strong $A-A$ and $A-B$ interactions, while decreased in the values of θ_3 and θ_4 represent weak $B-B$ interaction. The values of interionic distance and bond angles are graphically represented in Fig. 7.

3.2 Functional Group Analysis

The existence of two different vibrating modes corresponding to spinel lattice were detected by the spectroscopy technique FTIR. FTIR spectra for the nano ferrite powders were recorded within the range of $400\text{-}3000\text{ cm}^{-1}$ are represented in Fig. 8. FTIR spectroscopy is a spectroscopic method to obtain information about the position of the metal ions within the crystal lattice through the occurrence of different vibrational bands in the crystal lattice and also about cation distribution [62]. It can be seen from Fig. 8 that there are two major bands, which are reported in Table 6. The low-frequency absorption band is ν_2 , and the high-frequency

absorption band is ν_1 . The lower absorption frequency band for nano ferrite samples varies from 408.03 - 417.17 cm^{-1} and the upper-frequency band 542.32 - 555.69 cm^{-1} . The absorption bands, at a lower frequency, corresponds to the octahedral site and the high-frequency absorption bands correspond to the tetrahedral site within the spinel structure of nano ferrites [63].

The variation in positions is basically due to the difference in the bond length and bond strength of these different synthesized materials. The change in wavenumber may be due to the difference in radii of dopant La^{3+} (1.032 Å) and Fe^{3+} (0.64 Å), which affects $\text{Fe}^{3+}-\text{O}^{2-}$. Moreover, the different vibrational bands also occurred in the sample. The bands occurred around 1418 cm^{-1} because of the stretching vibration of nitrate ions [64], peaks around 1653 cm^{-1} attributed to the absorption of H-O-H group with bending vibration [65], the doublet peak at 2354 cm^{-1} is from ambient CO_2 gas [66].

3.3 Raman Analysis

Raman spectrum at RT for La^{3+} substituted Zn-Co nano ferrite was recorded within the range of 200-800 cm^{-1} and is depicted in Fig. 9. It was measured to study the vibrational properties. The spinel structure ferrites belong to $Fd-3m$ with eight formula units per unit cell. According to space group theory, the following set of optical phonon mode at Γ point of Brillouin zone exist in ferrites, i.e., $\Gamma = A_{1g}(R) + E_g(R) + T_{1g} + 3T_{2g}(R) + 2A_{2u} + 2E_u + 5T_{1u}(IR) + 2T_{2u}$ [67]. For the same vibrational mode, the existence of an inversion center in the Centro-symmetrical space group $Fd-3m$ indicates the mutual exclusion of Raman (R) and Infrared (IR) activities. $A_{1g}(R)$, $E_g(R)$, and $3T_{2g}(R)$ are the five first active modes detected in the Raman spectra. Notations A , E , T , and g represent one, two, three-dimension representation and symmetry to the center of inversion, respectively. In La^{3+} substituted nano ferrite samples (Fig. 9), five active modes are observed along with some additional vibrational modes that do not correspond to any of the active five modes [68, 69]. The presence of such modes corresponds to the dislocation, impurities, and lattice deformation in the lattice defects or crystal structure. However, since the results of XRD spectra show a single-phase structure, then the existence of such bands is considered as another confirmation of the crystal field deformation. Due to variation in polarizability during molecular vibration in the crystal field, which depends on a loss of symmetry, the Raman modes occur [69, 70]. In the spinel cubic structure ferrites, the five active modes corresponding to the motion of oxygen metal ions are reported in Table 7. A_{1g} is due to the symmetric stretch of FeO_4 and appears at 635.98-639.94 cm^{-1} . $T_{2g}(3)$ is due to symmetric and asymmetric bends of O^{2-} to Fe and appears at 508.83-

549.18 cm^{-1} . T_{2g} (2) seems at 404.95-468.71 cm^{-1} and is due to an antisymmetric stretching of Fe , and O^{2-} . E_g is symmetric bending of O^{2-} to Fe , and observed at 327.46-367.15 cm^{-1} . T_{2g} (1) appears at 286.19-314.78 cm^{-1} and is attributed to the translational motion of FeO [71, 72]. The broadening that occurs in the peaks is because of the asymmetric response of the crystal field, as seen by vibrating dipoles. Therefore, we assume that it increases the concept of the deformed crystal structure.

3.4 Current-Voltage (I-V) measurement analysis

The DC electrical resistivity of La^{3+} doped ZC nano ferrite samples was determined. The electrical properties of nanomagnetic materials are based on the sintering temperature, cation distribution at different lattice sites, and method of preparation [73]. The transition temperature after which the material's resistivity changes is known as the Curie temperature. The ferromagnetic region is the region below the Curie temperature. The region above the Curie temperature is paramagnetic. It was observed from Fig. 10 that the DC resistivity of all the samples increased as the temperature increased in the ferro region and decreased with increasing temperature in the para region. Samples where the DC resistivity reduces with rising temperature show semiconducting behavior. However, the band theory which describes the conduction process in semiconductor materials is not appropriate for soft ferrites. The polaron hopping mechanism is used to explain conduction in soft ferrites. It was observed in Fig. 11(a-d) that the DC resistivity is a minimum at $x = 0.05$ for the ferro and para region. It may be due to the presence of Fe^{2+} ions formed during sintering, as La^{3+} is added [74]. It was also clear from Fig. 11(a-c) that at $x = 0.1$ the DC resistivity is a maximum in the ferro and para regions. But above 503 K, the maximum resistivity was observed at $x = 0.0$ (Fig. 11(d)). This may be due to the increasing disorder in the structure.

Fig. 12 shows the variation of the $1000/T$ versus $\log \rho$ of the La^{3+} doped Zn-Co nano ferrite samples. Two regions are observed in the $\log \rho$ vs. $1000/T$ plots. The region below the Curie temperature (T_C) corresponds to the low activation energy region (Ferromagnetic region) and the region above Curie temperature (T_C) corresponds to the high activation energy region (Paramagnetic region) [73]. The determined value of the " T_C " for La^{3+} substituted samples is listed in Table 8. It was observed from Fig. 13 that the minimum value of " T_C " was 352 K for $x = 0.1$. The activation energy (ΔE) was calculated by taking the slope of $\log \rho$ vs. $1000/T$ (Arrhenius plots) using $\Delta E = 2.303 \times k_B \times 1000 \times slope (eV)$ [57]. The maximum activation energy (ΔE) was 1.7345 ± 0.0086 eV for $x = 0.1$, and variation with La^{3+}

concentration is reported in Fig. 13. It can be observed that activation energy (ΔE), which is in good agreement with the DC resistivity trend.

The drift mobility (μ_d) [57] of La³⁺ doped ZC nano ferrite samples as a function of temperature, is represented in Fig. 14. The calculated values of drift mobility (μ_d) at 313 K are reported in Table 8 and graphically as a function of La³⁺ concentration (x) are given in Fig. 13. They have the opposite trend with the DC resistivity because both drift mobility and DC resistivity are inversely related to each other.

3.5 UV-vis analysis

The optical band gap in nano ferrites depends on the following factors including dopant concentration, structure parameters, particle size, surficial effects, lattice strains, and impurities [75]. The UV-vis pattern of La³⁺ doped ZC ferrite samples is shown in Fig. 15. By employing the Tauc plot, the value of the optical band gap (E_g) of the as-prepared was determined. The optical band gaps (E_g) for $x = 0.0$ to $x = 0.125$ are reported in Table 8. It was clear from Table 8 that the optical band gaps (E_g) have a maximum value of 3.63 eV for $x = 0.1$.

3.6 Dielectric Analysis

Electrical dipoles form by the interaction of the charged di- and trivalent metal ions in the spinel matrix. The chemical composition, sintering temperature, distribution of metal ions among A - and B - sites, and methods of preparation are all responsible for the dielectric behaviour of iron oxide [76, 77]. To study the impact of the variation of La³⁺ cations, the dielectric constant (ϵ'), dielectric loss (ϵ''), dielectric tangent loss ($\tan \delta$), and ac conductivity (σ_{ac}) were determined as a function of applied frequency at RT for the La-doped Zn-Co nano ferrite samples. The variation between ϵ' and ϵ'' with the frequency for nano ferrite samples are shown in Fig. 16(a). At high frequency, both ϵ' and ϵ'' indicate variable values. But as the applied frequency is reduced both dielectric constant (ϵ') and loss (ϵ'') decrease. It can be seen in Fig. 16(a) that an abrupt decrease is observed in dielectric loss (ϵ'') but dielectric constant (ϵ') does not have a rapid decrease. Various researchers reported the same dielectric response in spinel ferrites and explained it based on the Maxwell Wagner's interfacial polarization theory [78, 79]. The degree of energy dissipation in the materials is known as a dielectric tangent loss ($\tan \delta$) [80]. The variation in $\tan \delta$ vs frequency for nano ferrite samples is represented in Fig. 16(b) within the frequency range 8 Hz to 8 MHz. It observed in Fig. 16(b) that the value of $\tan \delta$ is large at low frequency and small at high frequency. This is due to the grains with thinner boundaries that are more efficient at a low frequency as compared to the conducting grains, which cause higher dielectric tangent loss [80]. The variation between La³⁺

concentration and tangent loss is given in Fig. 17(a-c). It was observed in Fig. 17(a) at a low frequency that the dielectric tangent loss has minimum values as compared to other concentrations for a high concentration of La^{3+} ($x = 0.1$). But in the kHz and MHz frequency ranges sample $x = 0.1$ has a maximum value of tangent loss Fig. 17(b-c).

The measure of the ability to conduct an electric current in nano ferrite samples is known as ac conductivity (σ_{ac}) [80]. Fig. 18 indicates the graphical representation of the ac conductivity (σ_{ac}) as a function of frequency. It is observed in Fig. 18 there are two regions, i.e., low and high-frequency regions. The ac conductivity (σ_{ac}) increased with applied frequency for both low and high frequency. This phenomenon is characteristics of soft ferrites because the grain boundaries have low conductivity, and the grains are highly conductive[80].

3.6 Thermoelectric analysis

Fig. 19 shows the relation between the Seebeck voltage coefficient (S) with temperature for La^{3+} substituted Zn-Co nano-ferrite samples. The existence of more than one region shows the presence of more than one conduction process [81]. The Seebeck voltage coefficient (S) is divided into two groups, the first one of $x = 0.0-0.05, 0.125$, while the second is for $x = 0.075-0.1$. It observed that the charge carrier's variation between n- and p- types depend on the concentration (x) of La^{3+} cations. For the first group ($x = 0.0-0.05, 0.125$), it indicates that the conduction process is due to small positive polarons and gives a positive Seebeck voltage coefficient (S). In the second group, the conduction process is due to electrons and gives a negative Seebeck voltage coefficient (S). The positive values for samples $x = 0.0-0.05, 0.125$ show p-type materials while negative values for samples $x = 0.075-0.1$ indicate n-type materials. The power factor (PF) depends on the square of the Seebeck voltage coefficient (S^2) and electrical conductivity ($\sigma = 1/\rho$) [82-85]. The values of power factor (PF) calculated using $\text{PF} = S^2\sigma$ for La^{3+} substituted ZC nano-ferrites at 323 K, 423 K, and 523 K and graphically as given in Fig. 20.

3.7 Element compositional analysis

The elements within the chemical composition for La^{3+} substituted Zn-Co nano-ferrites were studied using energy dispersive X-ray (EDX) analysis. The elemental composition analysis for $\text{Zn}_{0.5}\text{Co}_{0.5}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ nano-ferrites is listed in Table 9. EDX pattern for $x = 0.0$ and $x = 0.025$, are given in Fig. 21. Zn, Co, Fe and O are the main elements in pure $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ observed and replaced by La^{3+} detected in samples $x = 0.025$ to $x = 0.125$. The EDX results indicated that the as-prepared samples did not contain any raw element. It also confirmed that the preparation of the iron oxygen was pure and La^{3+} cations doping achieved.

Conclusions

La³⁺ substituted Zn-Co samples were fabricated *via* the co-precipitation route. XRD analysis confirmed the as-prepared ferrites have a single-phase cubic matrix. The doping of La³⁺ leads to the increasing experimental lattice constant, and reduction in crystallite size. The X-ray density increased from 5.34 ± 0.01 to 5.56 ± 0.01 g/cm³ with the addition of La³⁺ ions. The average cationic radii and hopping lengths indicate a slight variation with increased dopant cations. The interionic distances were observed to decrease with a rise in dopant concentration. Also, the bond angles θ_1 , θ_2 , and θ_5 tend to be slightly enhanced, while θ_3 and θ_4 were observed to slightly reduce with the addition of La³⁺. Hence, the strength of *A–A* and *A–B* interactions increased, while *B–B* interaction decreased. FTIR spectra confirmed two major absorption bands, a low band (408.03-417.17 cm⁻¹) and a high band (542.32-555.69 cm⁻¹). However, Raman spectra showed *A*_{1g}, *E*_{1g}, and *3T*_{2g} five active modes and indicate symmetric and anti-symmetric behaviour of the vibrational band position of La³⁺ doped ZC nano ferrites. The DC resistivity and activation energies were determined from the electrical conduction process and it was observed that both have the same trend. Hence, drift mobility was found to be a minimum for $x = 0.1$. UV-vis analysis showed that the optical bandgap maximum for $x = 0.1$. Dielectric tangent loss indicates a momentous decreasing trend for Zn_{0.5}Co_{0.5}La_{0.1}Fe_{1.9}O₄ nanoparticles at low frequency. The study of the Seebeck voltage coefficient (*S*) and power factor (PF) imply that the as-prepared nano-ferrites are suitable for thermoelectric applications. The La³⁺ doped Zn-Co nano-ferrites were divided into n- and p-types semiconductors. EDX show the spatial distribution of elements as well as stoichiometry in all the samples.

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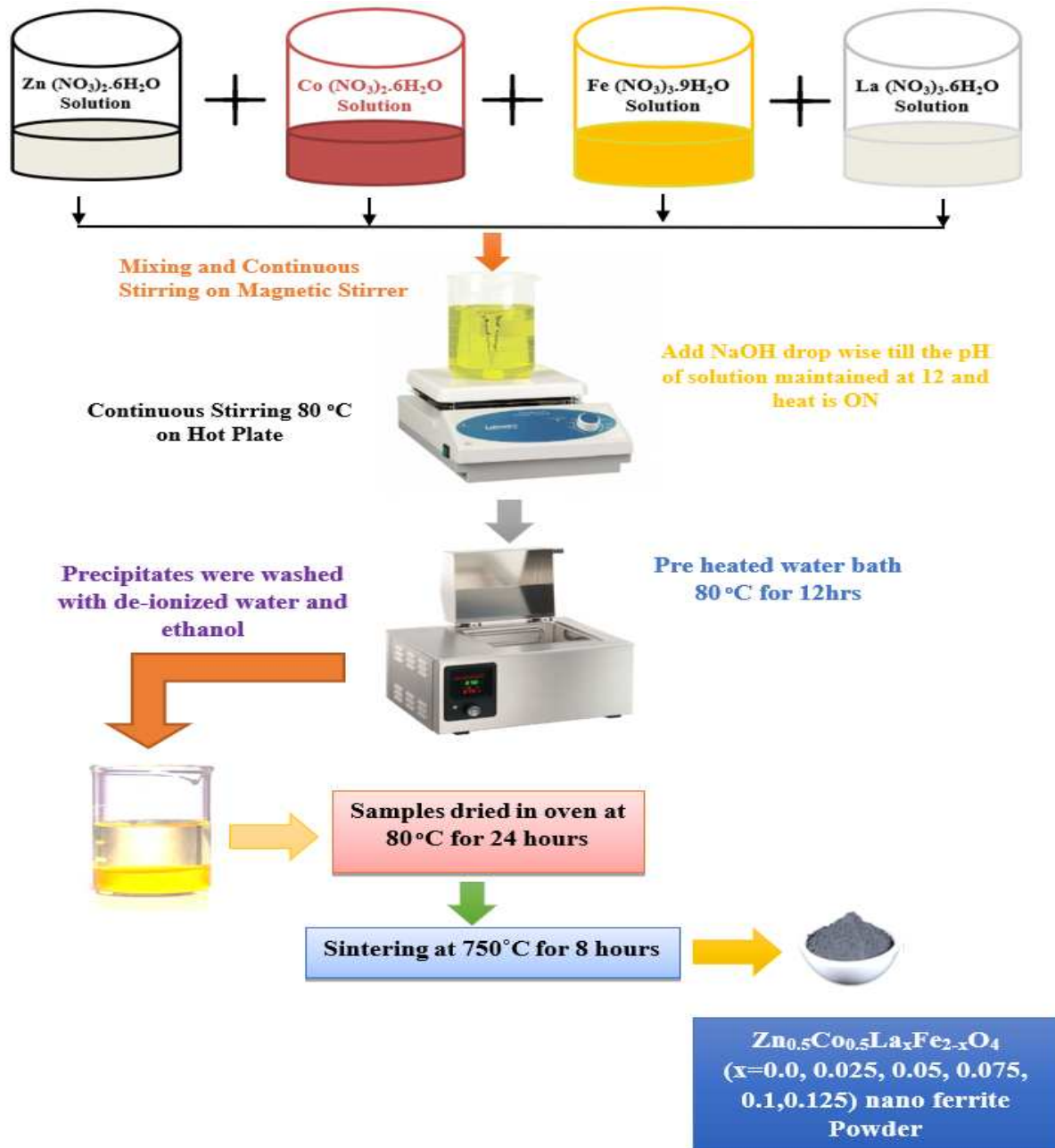


Fig. 1. Schematic diagram of the co-precipitation route for all the samples

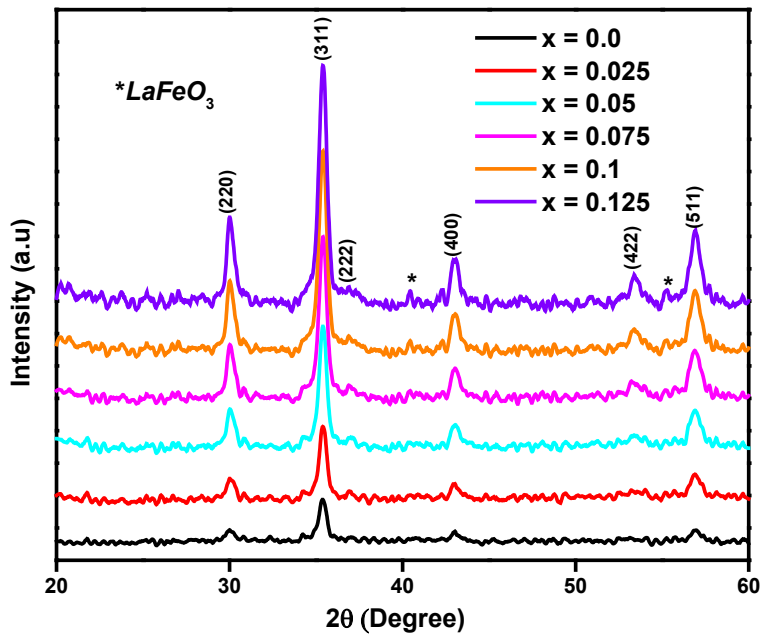


Fig. 2. XRD spectrum of La^{3+} doped Zn-Co nano ferrite powder

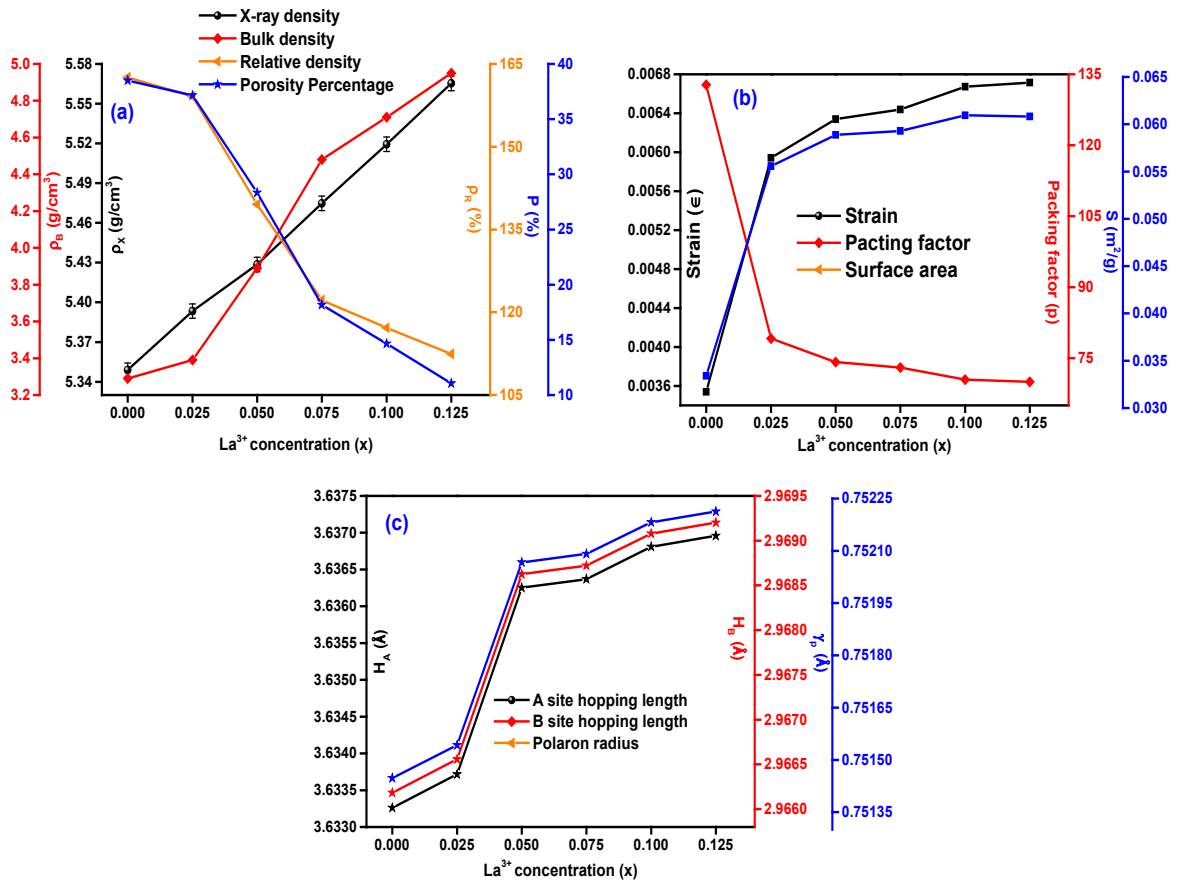


Fig. 3. La^{3+} concentration *versus* (a) X-ray, bulk, relative densities, and porosity percentage (b) strain, packing factor, and specific surface area (c) polaron radius, hopping length at *A* and *B* site

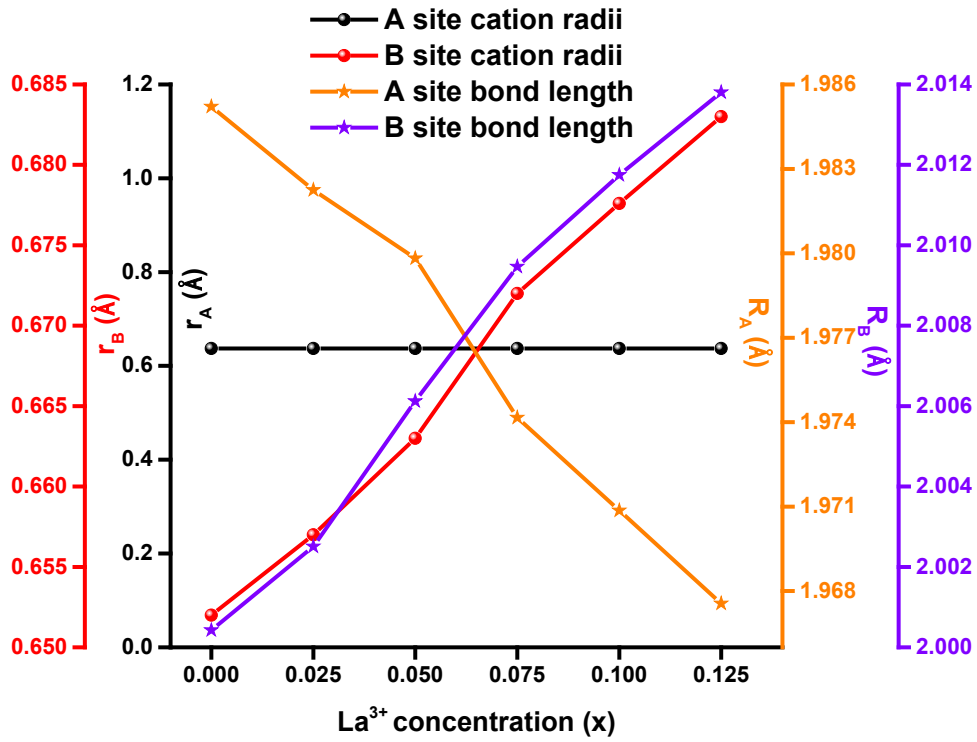


Fig. 4. A plot of La^{3+} concentration vs. cationic radii and bond lengths

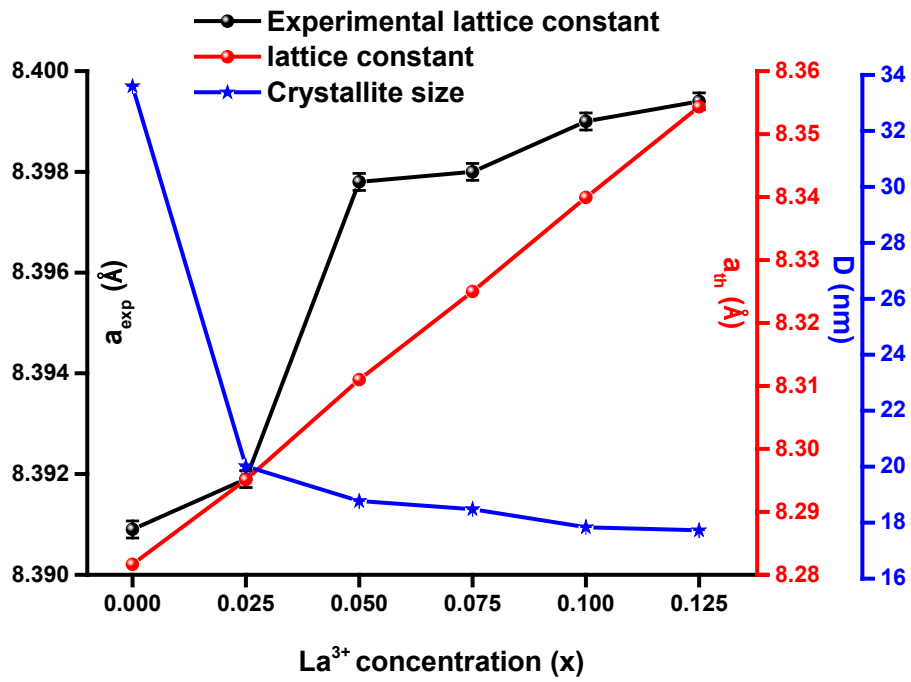


Fig. 5. A plot of La³⁺ concentration vs. crystallite size, experimental and theoretical lattice constants

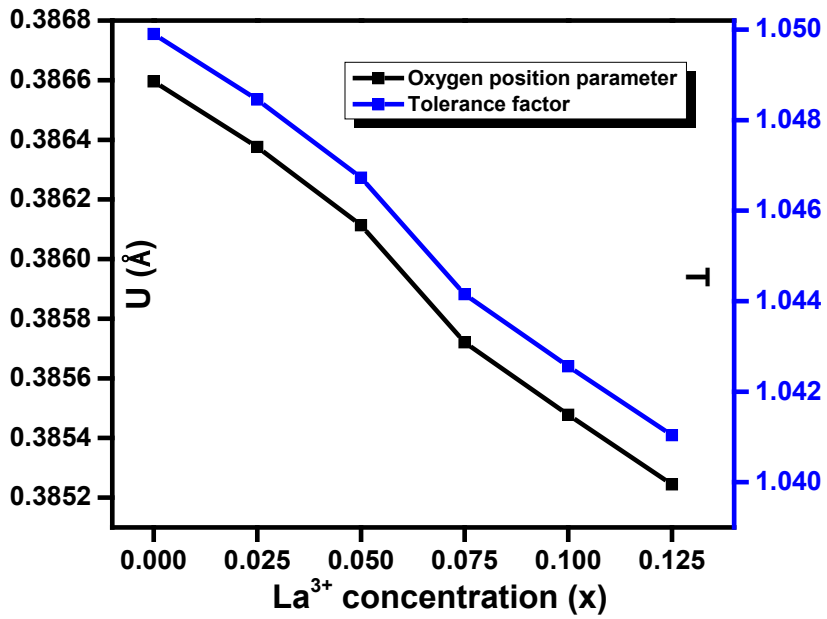
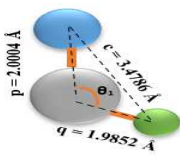


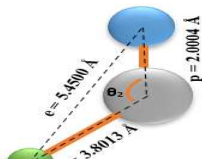
Fig. 6. A plot of La³⁺ vs. oxygen position parameter and tolerance factor

A–B Interaction

$x = 0.0$

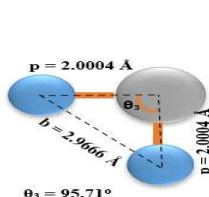


$\theta_1 = 121.57^\circ$

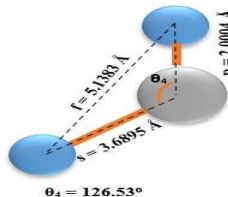


$\theta_2 = 137.71^\circ$

B–B Interaction

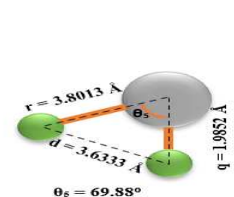


$\theta_3 = 95.71^\circ$



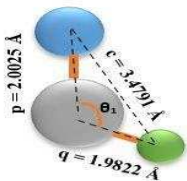
$\theta_4 = 126.53^\circ$

A–A Interaction

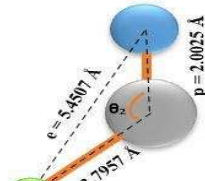


$\theta_5 = 69.88^\circ$

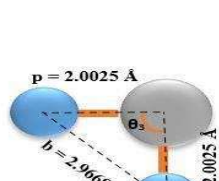
$x = 0.025$



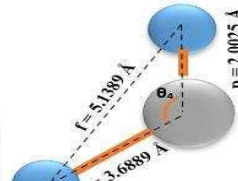
$\theta_1 = 121.64^\circ$



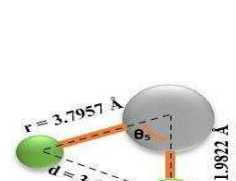
$\theta_2 = 137.97^\circ$



$\theta_3 = 95.60^\circ$

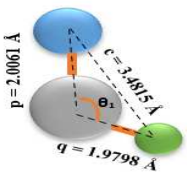


$\theta_4 = 126.51^\circ$

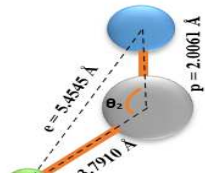


$\theta_5 = 70.05^\circ$

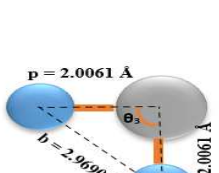
$x = 0.05$



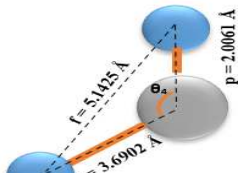
$\theta_1 = 121.72^\circ$



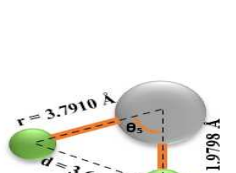
$\theta_2 = 138.28^\circ$



$\theta_3 = 95.46^\circ$



$\theta_4 = 126.48^\circ$



$\theta_5 = 70.26^\circ$

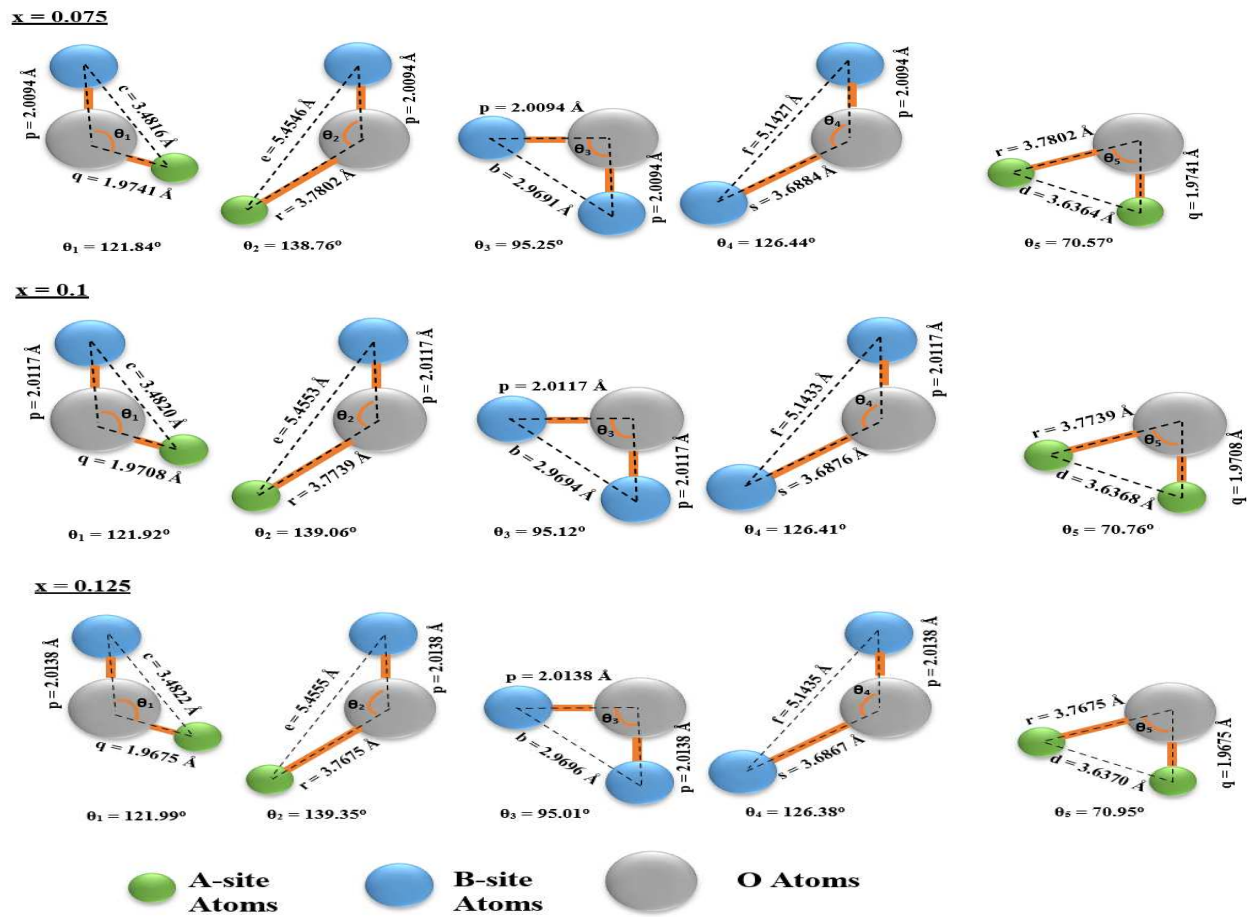


Fig. 7. The relation between interionic distance and bond angles

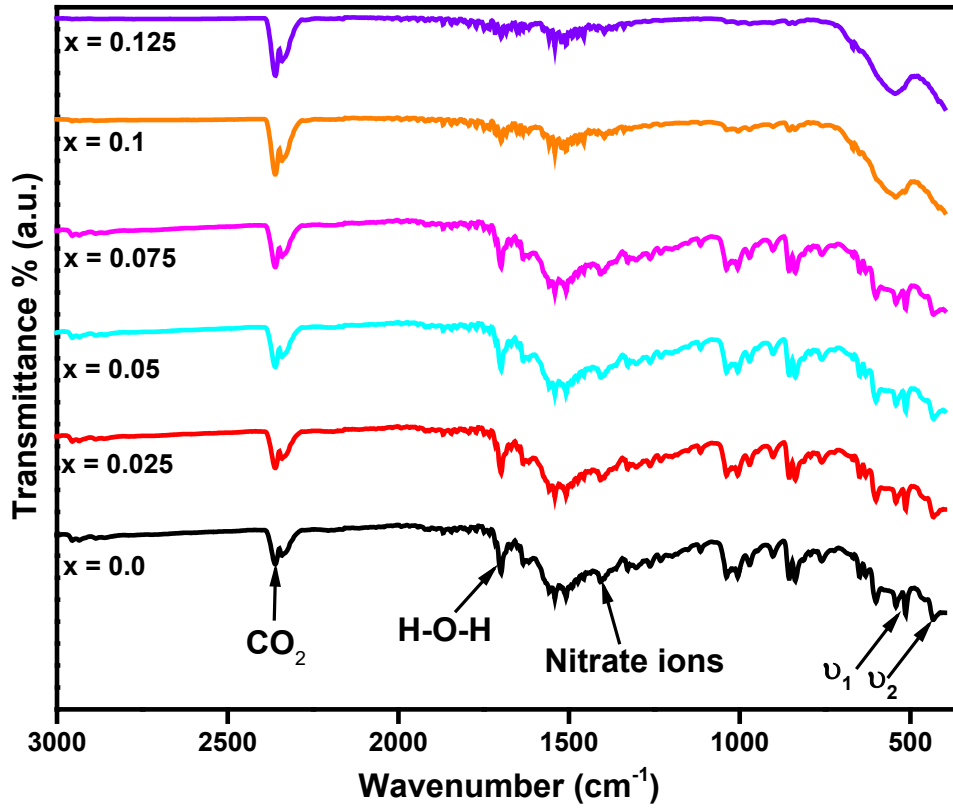


Fig. 8. La³⁺ doped ZC nano ferrite samples FTIR spectra

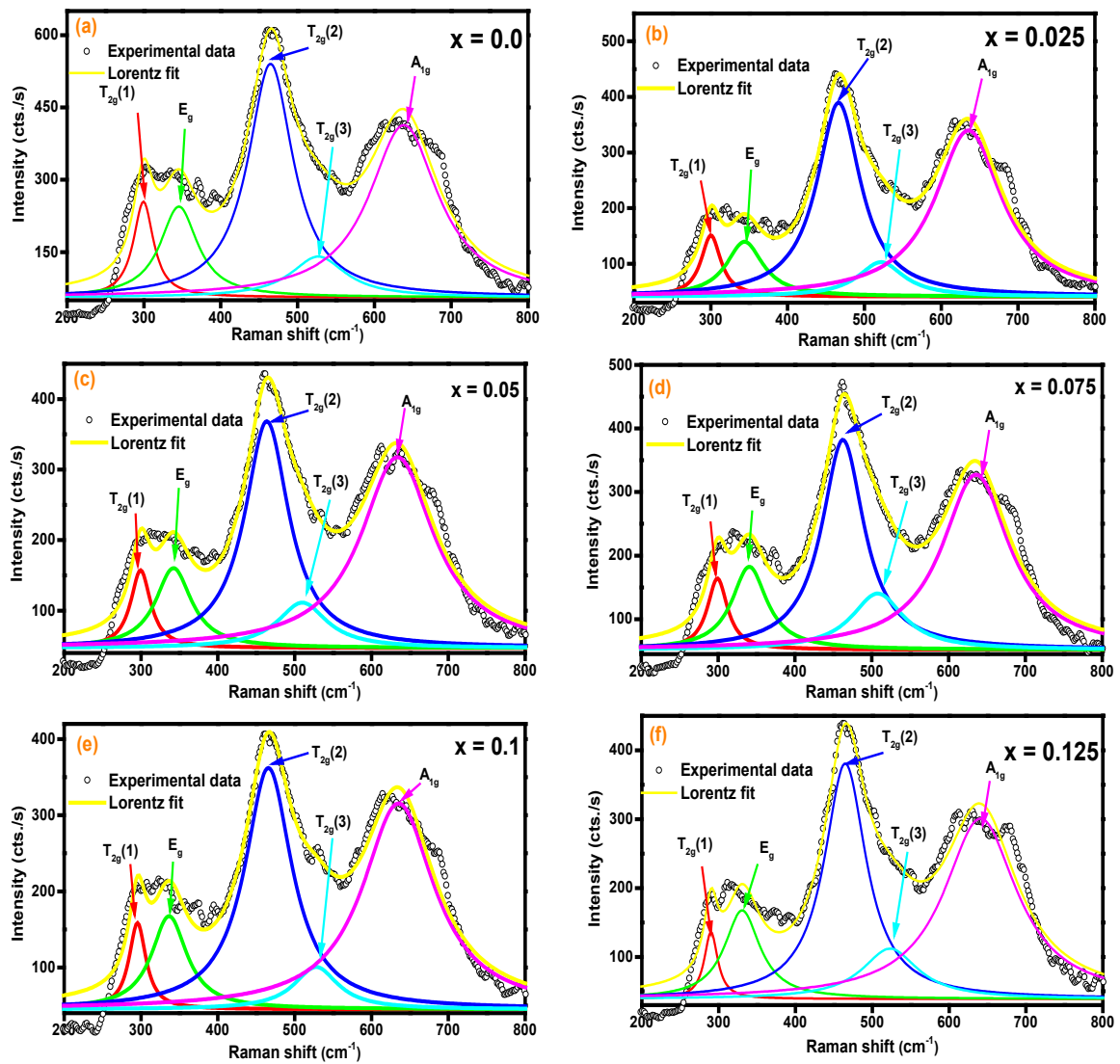


Fig. 9(a-f). Raman spectra of nano ferrite samples at room temperature

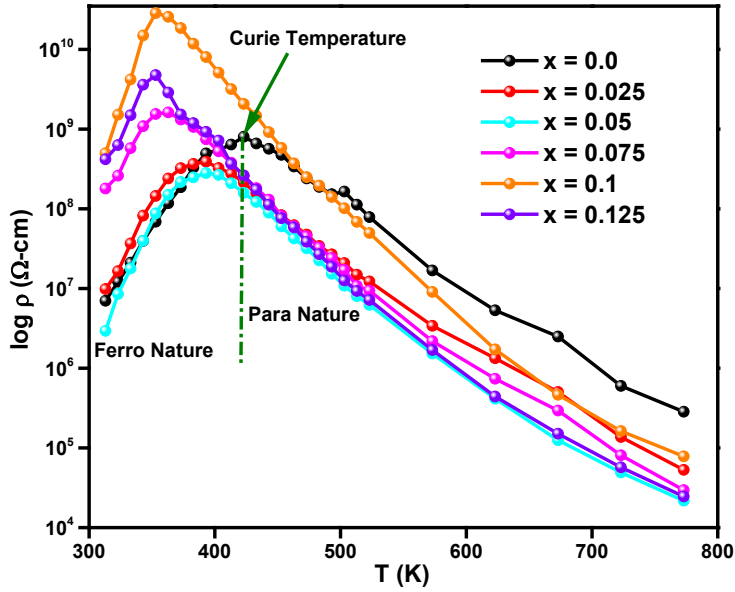


Fig. 10. Temperature vs. $\log \rho$ for La^{3+} doped ZC samples

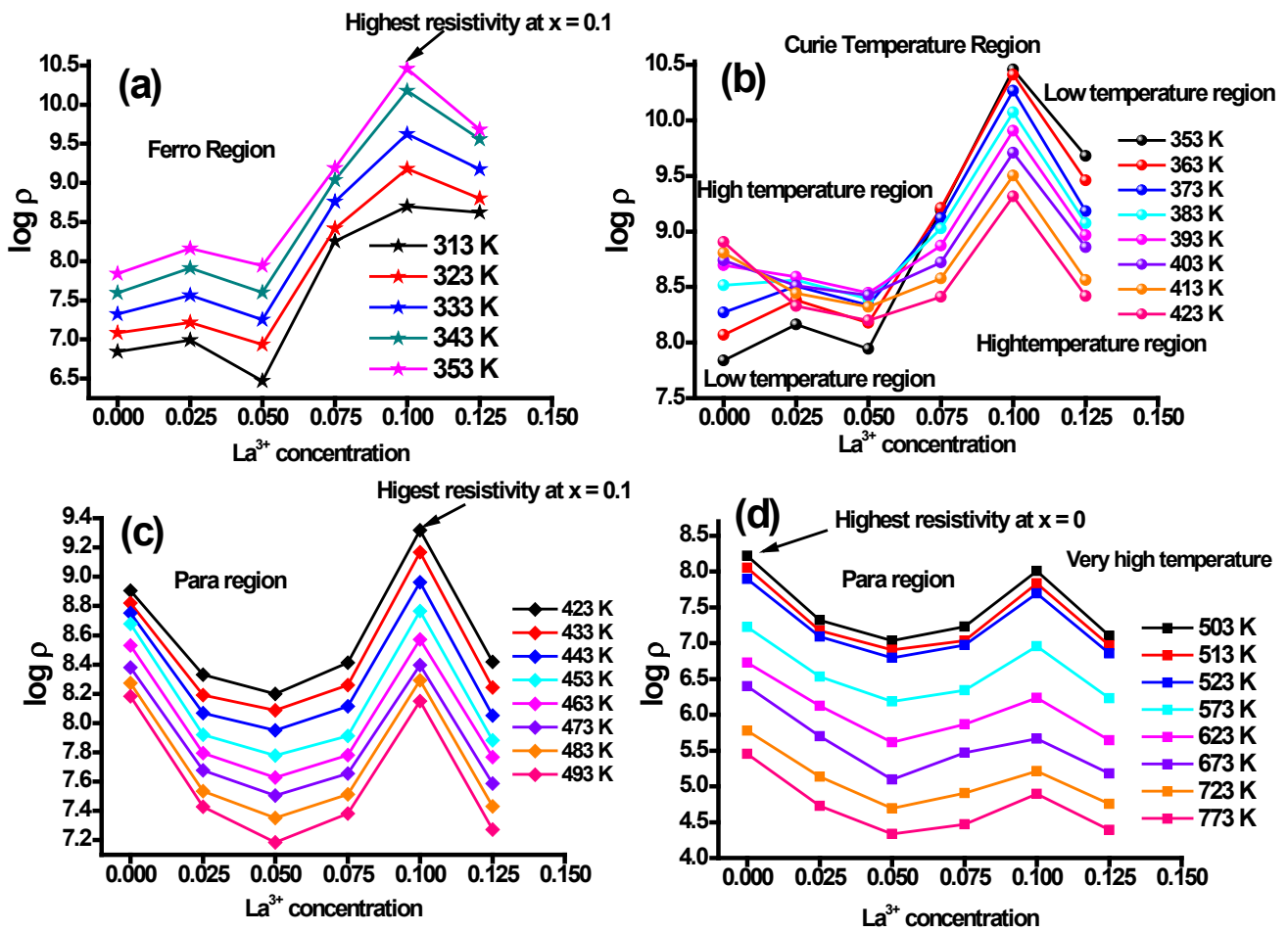


Fig. 11. Plots of La^{3+} concentrations vs. resistivity in ferro and para regions

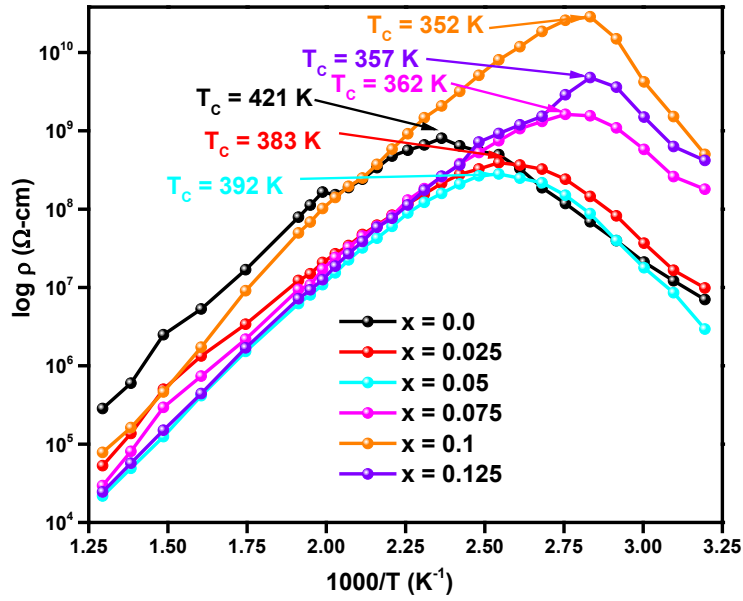


Fig. 12. $1000/T$ vs. $\log \rho$ of La^{3+} doped Zn-Co nano ferrite samples

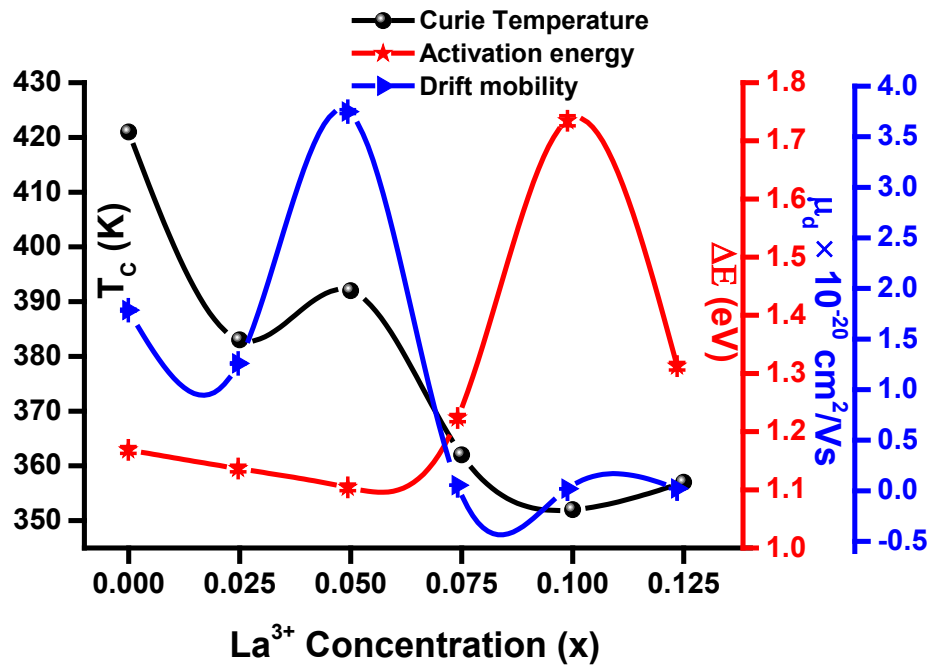


Fig. 13. La^{3+} vs. Curie temperature, activation energy, and drift mobility

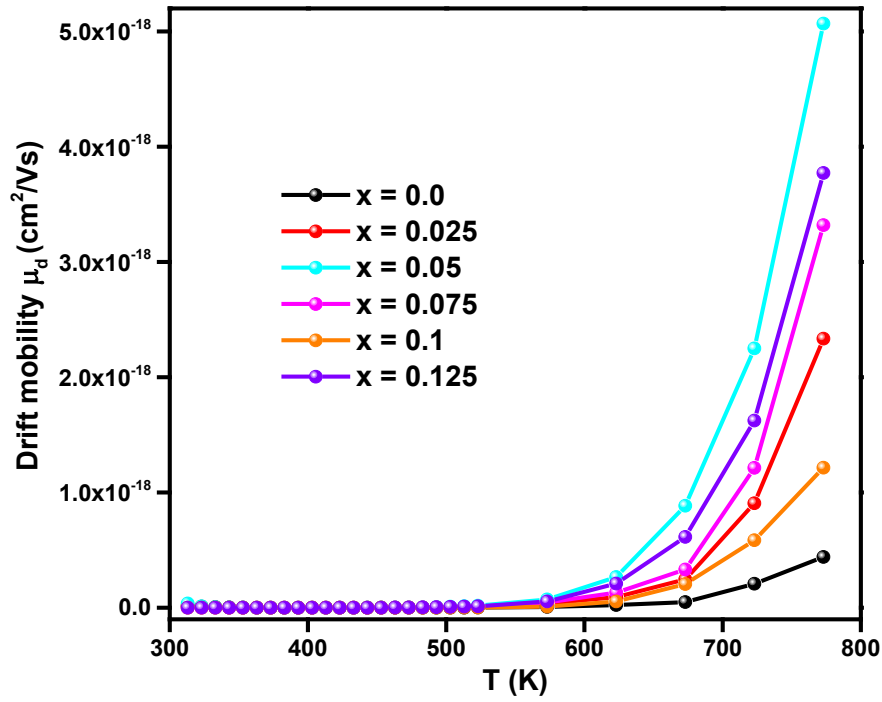


Fig. 14. Temperature vs. drift mobility of La^{3+} doped ZC nano-ferrites

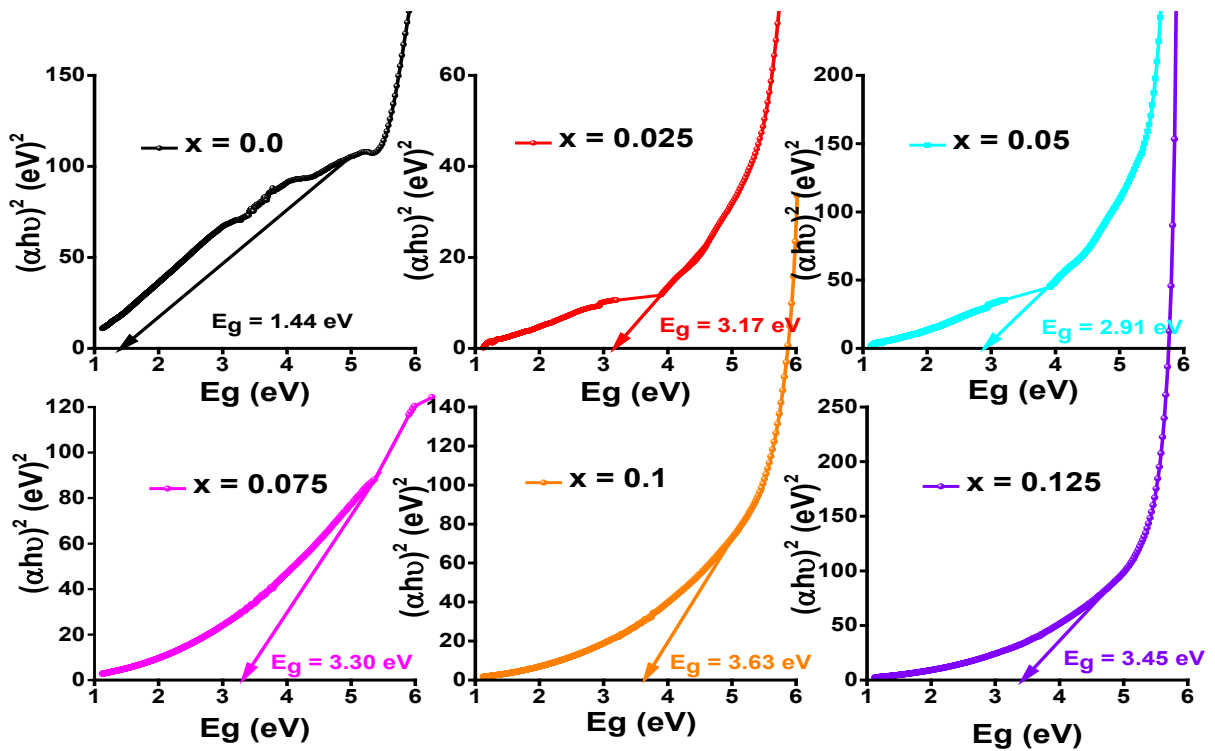


Fig. 15. Tauc plot for La^{3+} doped ZC ferrites

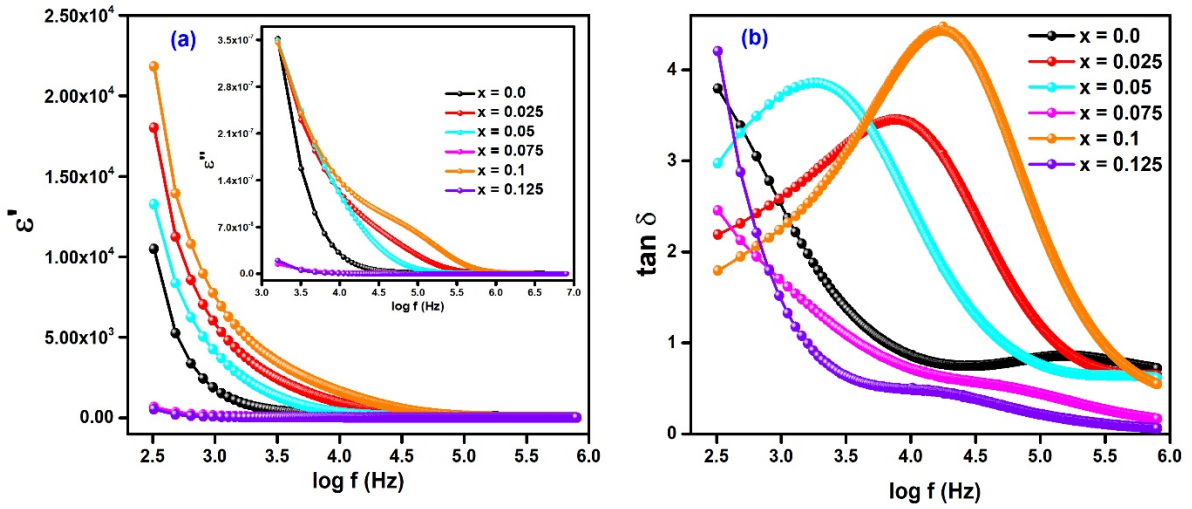


Fig. 16. $\log f$ versus (a) dielectric constant and loss for La³⁺ doped Zn-Co ferrites (b) tangent loss for La³⁺ doped ZC nano ferrites

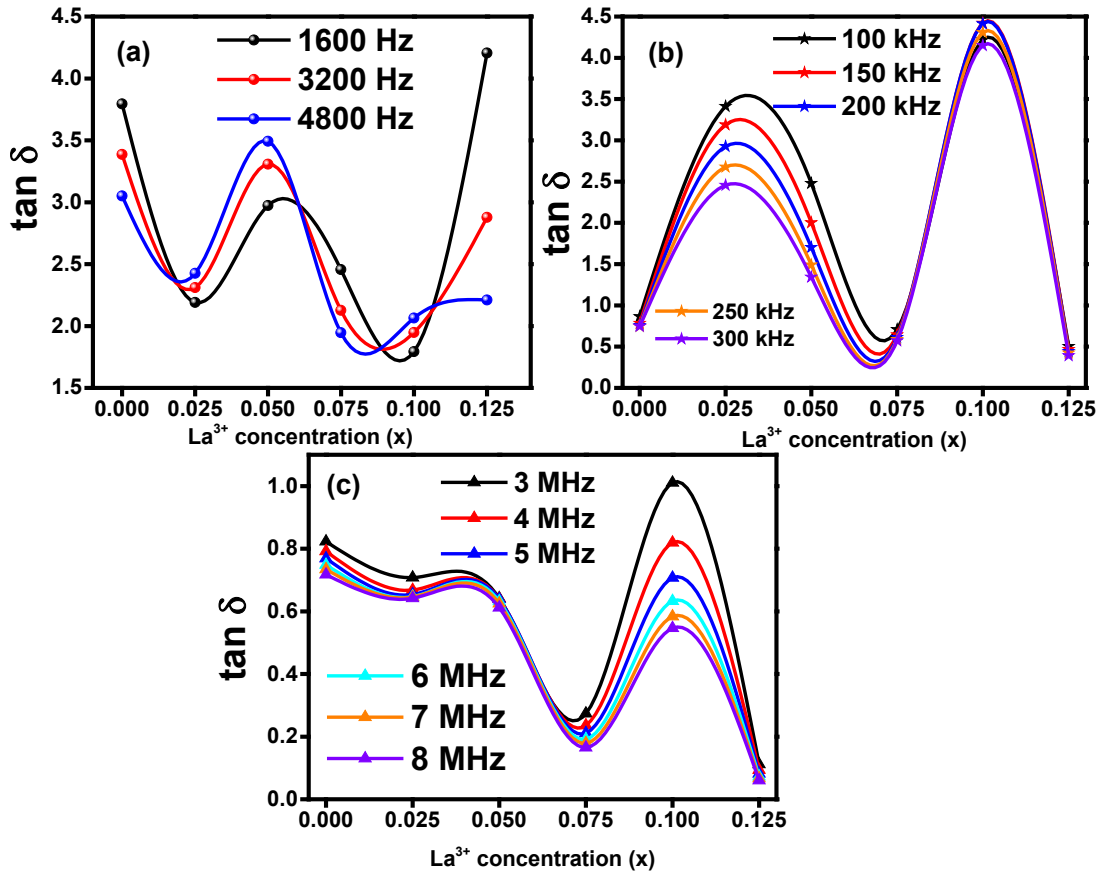


Fig. 17. La³⁺ concentration vs tangent loss at different frequencies

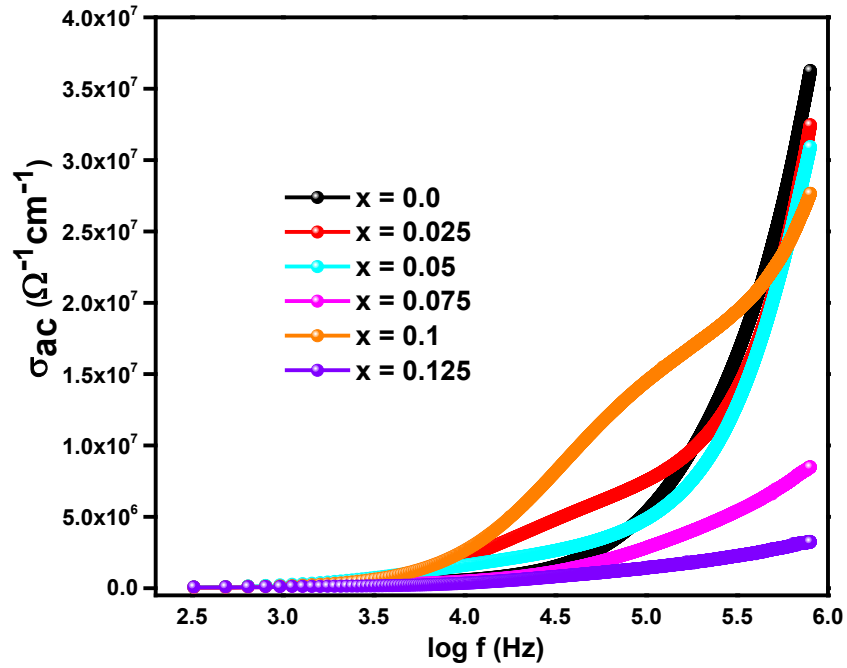


Fig. 18. The plot of log f vs ac conductivity of nano ferrite samples

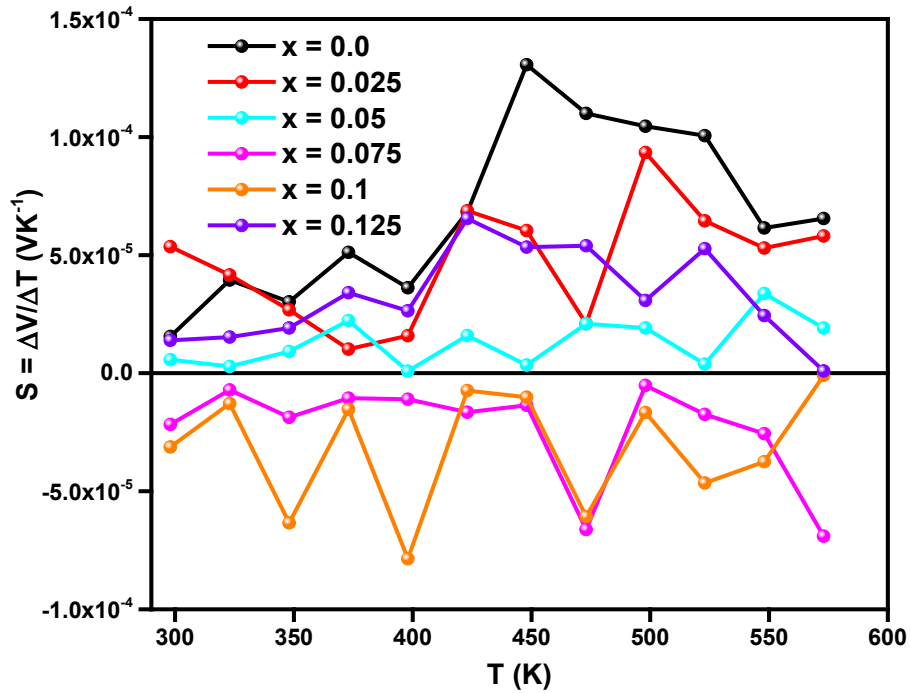


Fig. 19. The variation between temperature and Seebeck voltage coefficient

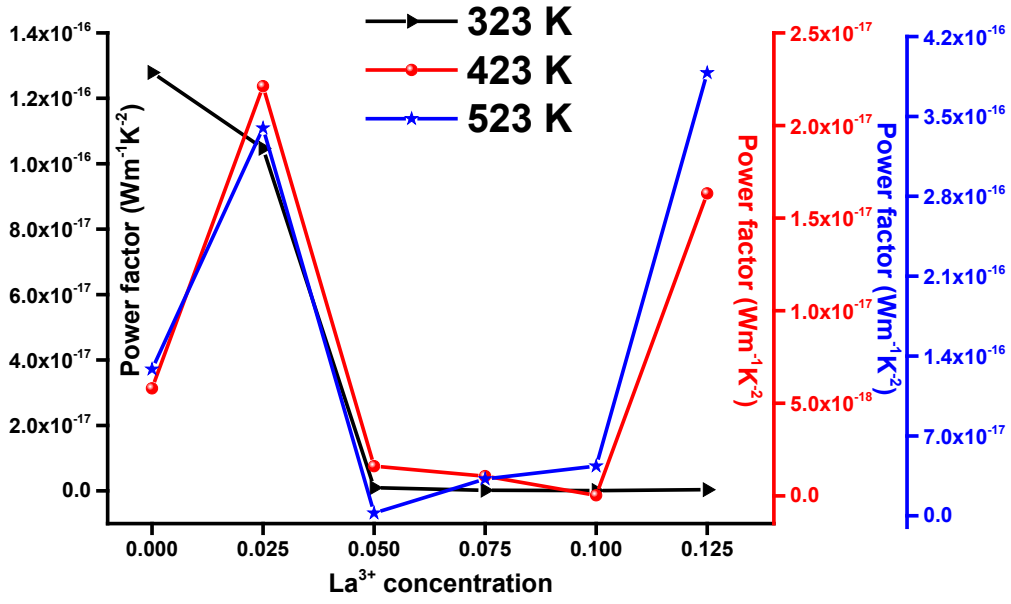


Fig. 20. The plot of La³⁺ concentration vs power factor at different temperatures

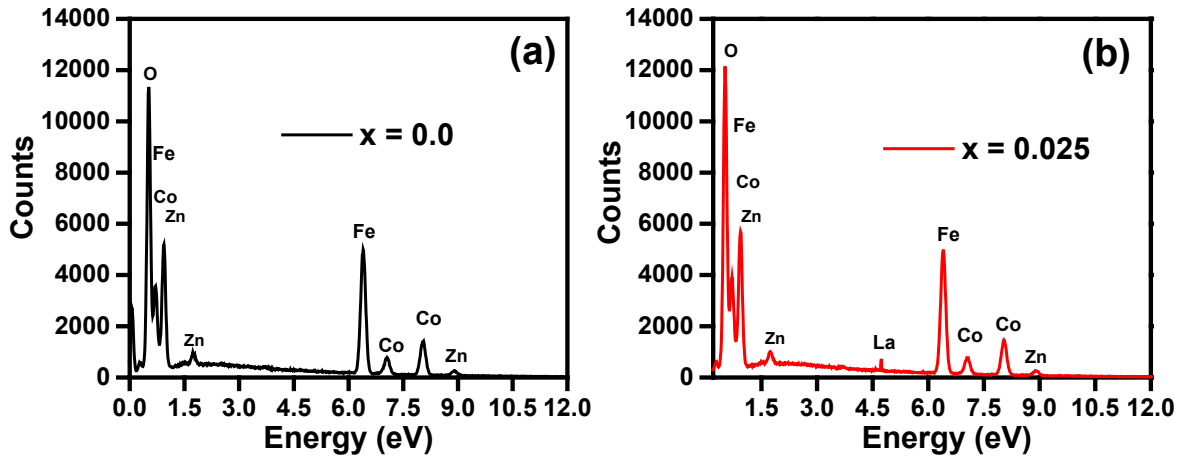


Fig. 21. EDX pattern for $x = 0.0$ and $x = 0.025$

Table 1: La³⁺ concentration (x), crystalline size (D), interplanar spacing (d), the experimental lattice constant (a_{exp}), dislocation line density (δ), unit cell volume (V), hopping length H_A , and H_B for La-doped ZC nano ferrites powder

x	$D \pm 0.1$ (nm)	d (Å)	a_{exp} (Å)	$\delta \times 10^{-4}$ (nm ⁻²)	V (Å) ³	H_A (Å)	H_B (Å)
0.000	33.6	2.5299	8.3909±0.0042	8.86	590.78	3.6332	2.9661
0.025	20.1	2.5302	8.3919±0.0042	25.0	591.00	3.6337	2.9665
0.050	18.7	2.5320	8.3978±0.0042	28.4	592.24	3.6362	2.9686
0.075	18.4	2.5321	8.3980±0.0042	29.3	592.29	3.6363	2.9687
0.100	17.8	2.5324	8.3990±0.0042	31.4	592.51	3.6368	2.9690
0.125	17.5	2.5325	8.3994±0.0042	31.8	592.58	3.6369	2.9692

Table 2: Molecular weight (M), X-ray (ρ_x), bulk (ρ_B) and relative (ρ_R) densities, porosity (P) percentage, packing factor (p), strain (ε), specific surface area (S), and polaron radius (γ_p) for nano ferrites samples

x	M (g/mol)	$\rho_x \pm 0.01$ (g/cm ³)	ρ_B (g/cm ³)	ρ_R (%)	P (%)	p	ε	S (cm ² /g)	γ_p (Å)
0.000	237.79	5.34	3.29	162.57	38.38	132.77	0.0035	0.0333	0.7514
0.025	239.86	5.39	3.39	159.09	37.10	79.11	0.0059	0.0555	0.7515
0.050	241.93	5.42	3.89	139.55	28.22	74.14	0.0063	0.0588	0.7520
0.075	244.01	5.47	4.48	122.20	18.09	73.00	0.0064	0.0592	0.7520
0.100	246.09	5.51	4.71	117.18	14.51	70.43	0.0066	0.0609	0.7521
0.125	248.17	5.56	4.95	112.43	11.05	69.98	0.0067	0.0608	0.7522

Table 3: Theoretical structural parameters for as-prepared samples

x	r_A (Å)	r_B (Å)	a_{th} (Å)	U (Å)	T	R_A (Å)	R_B (Å)	R_x (Å)	$R_{x'}$ (Å)	$R_{x''}$ (Å)
0.000	0.637	0.652	8.2816	0.3866	1.0499	1.9852	2.0004	3.2418	2.6914	2.9730
0.025	0.637	0.657	8.2951	0.3863	1.0484	1.9822	2.0025	3.2370	2.6969	2.9731
0.050	0.637	0.663	8.3109	0.3861	1.0467	1.9798	2.0061	3.2330	2.7051	2.9749
0.075	0.637	0.672	8.3249	0.3857	1.0441	1.9741	2.0094	3.2237	2.7144	2.9746
0.100	0.637	0.677	8.3399	0.3854	1.0425	1.9708	2.0117	3.2184	2.7205	2.9747
0.125	0.637	0.683	8.3543	0.3852	1.0410	1.9675	2.0138	3.2130	2.7262	2.9746

Table 4: Interionic distance between the ions for all the samples

x	p (Å)	q (Å)	r (Å)	s (Å)	b (Å)	c (Å)	d (Å)	e (Å)	f (Å)
0.000	2.0004	1.9852	3.8013	3.6895	2.9666	3.4786	3.6333	5.4500	5.1383
0.025	2.0025	1.9822	3.7957	3.6889	2.9669	3.4791	3.6338	5.4507	5.1389
0.050	2.0061	1.9798	3.7910	3.6902	2.9690	3.4815	3.6363	5.4545	5.1425
0.075	2.0094	1.9741	3.7802	3.6884	2.9691	3.4816	3.6364	5.4546	5.1427
0.100	2.0117	1.9708	3.7739	3.6876	2.9694	3.4820	3.6368	5.4553	5.1433
0.125	2.0138	1.9675	3.7675	3.6867	2.9696	3.4822	3.6370	5.4555	5.1435

Table 5: Calculated values of bond angles for La-doped Zn-Co nano ferrites samples

x	θ_1	θ_2	θ_3	θ_4	θ_5
0.000	121.57	137.71	95.71	126.53	69.88
0.025	121.64	137.97	95.60	126.51	70.05
0.050	121.72	138.28	95.46	126.48	70.26
0.075	121.84	138.76	95.25	126.44	70.57
0.100	121.92	139.06	95.12	126.41	70.76
0.125	121.99	139.35	95.01	126.38	70.95

Table 6: Absorption bands of as-prepared samples

x	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)
0.000	542.32	408.03
0.025	543.46	408.18
0.050	544.18	410.43
0.075	545.67	408.33
0.100	555.69	416.63
0.125	543.88	417.17

Table 7: At room temperature Raman modes for La³⁺ doped ZC samples

x	Raman shift (cm ⁻¹)				
	T_{2g} (1)	E_g	T_{2g} (2)	T_{2g} (3)	A_{1g}
0.000	299.35	345.56	464.86	526.95	638.25
0.025	300.16	344.02	466.53	521.62	635.38
0.050	299.45	342.34	463.79	509.93	633.81
0.075	299.11	340.71	462.49	507.72	635.60
0.100	295.39	336.66	465.85	527.86	635.12
0.125	289.99	330.59	464.78	523.08	640.83

Table 8: Values of La³⁺ concentration, resistivity, activation energy, Curie temperature, drift mobility, and optical bandgap for La³⁺ substituted Zn-Co nano-ferrites

x	ρ at 313 K $\times 10^8$ (Ω cm)	ΔE (eV)	T_C (K)	$\mu_d \times 10^{-20}$ at 313 K (cm ² V ⁻¹ s ⁻¹)	E_g (eV)
0.000	0.0700 \pm 0.0035	1.1686 \pm 0.0058	421	1.7857 \pm 0.0089	1.44
0.025	0.0985 \pm 0.0049	1.1364 \pm 0.0056	383	1.2583 \pm 0.0063	3.17
0.050	0.0294 \pm 0.0015	1.1042 \pm 0.0055	392	3.7479 \pm 0.0187	2.91
0.075	1.7978 \pm 0.0899	1.2233 \pm 0.0061	362	0.0544 \pm 0.0003	3.30
0.100	4.9919 \pm 0.2496	1.7345 \pm 0.0086	352	0.0195 \pm 0.0001	3.63
0.125	4.1843 \pm 0.2092	1.3125 \pm 0.0065	357	0.0221 \pm 0.0001	3.45

Table 9: Elemental composition for La³⁺ substituted Zn-Co nano-ferrites

Samples	Elements present (mol)				
	Zn	Co	La	Fe	O
<i>Zn_{0.5}Co_{0.5}Fe₂O₄</i>	7.43	6.67	-	30.67	55.23
<i>Zn_{0.5}Co_{0.5}La_{0.025}Fe_{1.975}O₄</i>	7.13	6.50	0.06	29.57	56.74
<i>Zn_{0.5}Co_{0.5}La_{0.05}Fe_{1.95}O₄</i>	7.94	6.20	0.69	28.86	56.31
<i>Zn_{0.5}Co_{0.5}La_{0.075}Fe_{1.925}O₄</i>	8.37	7.78	0.94	24.75	58.16
<i>Zn_{0.5}Co_{0.5}La_{0.1}Fe_{1.9}O₄</i>	8.94	7.37	1.07	25.23	57.39
<i>Zn_{0.5}Co_{0.5}La_{0.125}Fe_{1.875}O₄</i>	8.70	6.47	1.11	24.17	59.55