Effect of Ce^{3+} substitution on the structural, morphological, dielectric, and impedance spectroscopic studies of Co–Ni ferrites for automotive applications

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Abstract: Cerium (Ce^{3+})-substituted cobalt–nickel (Co–Ni) ferrite nanostructures of spinel cubic phase with space group $Fd\bar{3}m$ had been successfully engineered by solution combustion route. The effect of Ce^{3+} substitution on the structural, morphological, dielectric, and impedance spectroscopic investigations are probed by using X-ray diffraction (XRD), scanning electron microscope (SEM), and impedance analysis, respectively. Rietveld refinement of XRD data reveal that samples exhibit well-crystalline nature with single phase. The microstructural realm with various Ce^{3+} doping levels has been identified from SEM micrographs. The replacement of Fe^{3+} by Ce^{3+} cations has been confirmed by using energy-dispersive analysis of the ferrite samples. The dielectric constant (ϵ'), dielectric loss ($\tan\delta$), ac conductivity (σ_{ac}), and impedance (Z' and Z'') at room temperature is investigated as a function of frequency, respectively. The variation of dielectric properties ϵ' , $\tan\delta$, σ_{ac} with frequency are explained by Maxwell–Wagner type of interfacial polarization and the hopping of charge between Fe^{2+} and Fe^{3+} as well as the dopant ions at B-sites. The decrease in dielectric constant and dielectric loss tangent with frequency follows the phenomenon of Debye's relaxation. The enhancement in AC conductivity with frequency is proportional to Ce^{3+} concentration which follows Jonscher law. The complex impedance plots (Z' vs. Z'') allows to determine the contribution for conductivity either from grain or grain boundary. Complex electric modulus plot (M' vs. M'') provides the validation to the result drawn from the complex impedance plots. The results indicate the existence of non-Debye type of relaxation in these ferrites. Impedance spectroscopy allows the ferrite materials to estimate electrical properties which arise due to hopping and relaxation phenomena.

Keywords: Co–Ni ferrites; Solution combustion method; Dielectric constant; Electric modulus; Ac conductivity

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1. Introduction

Ferrites are the class of materials which exhibits diverse properties very much useful for technological and scientific applications. The ferrite has spinel cubic structure imposing their domains in electronic, mechanochemical, photocatalytic,

magnetic, and biological applications [1, 2]. At suitable large frequencies, they exhibit large saturation magnetization, large permeability, suitably high electrical resistivity, low dielectric constant, and low dielectric loss, which are some indistinguishable features of these materials put into solid-state and magnetoelectronics [3, 4]. The physical property of the ferrites depends on method of synthesis, dopants chosen, concentration of the dopants, and the site for which the dopant is used. The polycrystalline ferrites like nickel ferrites with small quantity of rare earth doping have low dielectric loss

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and high resistivity, and due to these properties, they have wide application such as microwave devices and transformer core applications [5, 6]. The NiFe_2O_4 , a soft ferrite material, finds diverse applications to be used as gas sensors for good absorption, catalysts, ferrofluids, and recording media with high density [7, 8]. Cobalt ferrite, CoFe_2O_4 , exhibits high coercivity with high chemical stability and moderate magnetization due to semi-hard magnetic material, and therefore, it is useful for recording applications [9–12]. Thus the spinel ferrite is very useful application such as in microwave devices, high-density magnetic recording, and magnetic fluids [13, 14]. According to Neel's model, ferrites crystallize with two magnetic sub-lattices, i.e., tetrahedral (A) sites and octahedral (B) sites. The properties of ferrites are mainly depending on the distribution of cations in A- and B-sites and their valence state [15]. The electrical and dielectric properties of ferrites can be tuned by the rare earth substitution at the A- and B-sites of the ferrite [16]. From this knowledge, it is possible to introduce different metallic ions to these ferrites to enhance their electronic and magnetic properties appreciably. A large number of researchers and research teams around the globe have realized in order to synthesize, to study the properties and to observe the effect of various additives on their properties. Additives play an important role to modify the microstructure and properties of the samples [17]. The present study aims to the study of effect of larger ionic radius on Ce^{3+} substitution on $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ with $x = 0.0, 0.01, 0.015, 0.02, 0.025$, and 0.03 to describe the structural, microstructural, and dielectric properties in detail.

2. Experimental

Ce^{3+} -substituted Co–Ni ($\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ (here $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03) nanoferrite was synthesized via solution combustion chemistry route. The precursors used are all the metal nitrates of AR grade, e.g., cobaltous nitrate hexahydrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, nickel nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, ferrous nitrate nanohydrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$, and cerium nitrate hexahydrate $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ as oxidizers. We have used urea and glucose mixture to serve as fuel. The ratio of oxidizers to that of fuel is maintained unity. The stoichiometric quantities of metal nitrate (oxidizers) and fuel mixture were dissolved in demineralized water. All the precursors in a borosil beaker kept on a magnetic stirrer for about 25 min maintained at 500 rpm until the solution becomes homogeneous. This solution is introduced into a pre-heated muffle furnace maintained at 450°C . The solution first boils and then more volatile solvents get escaped from the solution; the resultant mass get ignited rigorously yields foamy, puffy black powder of Co–Ni ferrite. The combustion process takes less than 20 min. The

voluminous powder of Co–Ni ferrite is ultra-fine-grinded. The obtained fine powder is mixed with 1% PVA binder and made pellets by pressing it at a pressure of 5 ton per square centimeter for about 5 min, and they are sintered at 800°C for 2 h in a furnace. Preliminary characterization for phase confirmation of synthesized samples is done using XRD, PANalytical X'Pert Pro diffractometer with CuK_α ($\lambda = 1.54 \text{ \AA}$) radiation at room temperature. Surface morphology is scrutinized using a JEOL JSM-6390LV scanning electron microscope (SEM). The flat surfaces of sintered pellets are covered with silver paste to make good electrical connection. The impedance spectroscopy data collection is carried out for the ferrite samples in the frequency range up to 20 MHz at room temperature using LCR Hi-Tester impedance spectrometer.

3. Results and discussion

3.1. Structural properties of $\text{Co}_{0.5}\text{Ni}_{0.5}$ ferrites doped with Ce^{3+}

3.1.1. XRD results of $\text{Co}_{0.5}\text{Ni}_{0.5}$ ferrites doped with Ce^{3+}

Rietveld refined XRD patterns for $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ (here $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03) is depicted in Fig. 1. It is very clear that the major peaks of the XRD pattern is indexed as 220, 311, 222, 400, 422, 511 and 440. XRD patterns of as-synthesized samples are in good match with standard reference patterns of the typical spinel cubic ferrite.

The non-occurrence of additional peaks indicates that there is no impurity pick up during synthesis process. GSAS program is used to fit all the peaks of XRD pattern. The χ^2 values of the fitted curves are found low as mentioned in Table 1. The R_p and R_{wp} called as residue factors are less than 0.1. This result tells a good agreement exists between the calculated and observed diffraction pattern. Peak width of (311) peak is used to estimate the crystallite size of the as-synthesized samples using Debye–Scherrer formula [18].

$$D_{hkl} = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where D_{hkl} is the crystallite size in nanometers, k is the Scherrer constant taken as 0.94; β is the full width at half maximum (FWHM), θ is the Bragg's angle and λ is the wavelength of X-rays. The crystallite size of the ferrite particles for the (311) major peak lies in the range 24–32 nm and are given in Table 1. Lattice parameter 'a' is determined using relation [19].

$$a = \frac{\lambda(h^2 + k^2 + l^2)^{\frac{1}{2}}}{2 \sin \theta} \quad (2)$$

Fig. 1 Rietveld refined XRD patterns of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ ferrite nanoparticles, where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03

Table 1 Structural parameters acquired via Rietveld refined XRD results of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ (where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03) ferrite nanoparticles

Ce^{3+} content x	Crystallite size (nm)	Lattice parameter (Å)	χ^2 from Rietveld refinement	Internal strain $\times 10^{-4}$ (%)	X-ray density (g/cm ³)	Grain size (nm)
0.0	35	8.31324	1.37	27.1	5.326	38
0.01	27	8.35876	1.56	29.5	5.353	50
0.015	32	8.35844	1.90	35.5	5.363	50
0.02	26	8.35805	1.48	37.3	5.373	50
0.025	24	8.35791	1.40	39.8	5.383	48
0.03	25	8.35779	1.23	39	5.393	48

Here (h k l) are Miller indices of the respective peaks of the XRD pattern. The lattice parameter is found to decrease with addition of Ce^{3+} content which is attributed as follows. The inclusion of larger ionic radii Ce^{3+} (1.14 Å) at the site of Fe^{3+} (0.63 Å) of Co–Ni spinel ferrite lowers the lattice parameter from 8.35876 to 8.35779 Å, and this is due to internal strain which makes perturbations in the

$\text{Ce}^{3+}\text{--O}^{2-}$ bonds and anisotropy in the crystallinity. To overcome the crystalline anisotropy and internal strain, lattice parameter and crystallite size decrease. In other words, Fe^{3+} in spinel ferrites has the probability of occupying tetrahedral (A-site) or Octahedral (B-site). Substitution of Ce^{3+} has the tendency to occupy the octahedral site. Ce^{3+} substitution at Fe^{3+} site demands larger energy

of activation to enter the octahedral sites as $\text{Ce}^{3+}-\text{O}^{2-}$ instead of occupying Fe^{3+} sites, and Ce^{3+} sits at the interstitial sites and creates an excess stress resulting in the decrease in crystallite size and lattice parameter. The trend of lattice parameter and crystallite size with Ce^{3+} content is represented pictorially as in Fig. 2.

X-ray density can be calculated as [20]

$$\rho = \frac{ZM_w}{N_A a^3} \quad (3)$$

Here M_w is the molecular weight, $Z = 8$ is the number of molecules per unit cell, N_A is Avogadro number and 'a' is the lattice parameter. X-ray density increasing with increase in Ce^{3+} content in the samples is due to larger mass of Cerium ion as compared to Fe^{3+} and also decreases in lattice parameter. Internal strain (ε) produced in the samples were estimated using Williamson–Hall relation [21].

$$\varepsilon = \frac{\beta_{hkl}}{\tan \theta} \quad (4)$$

The graphical variation of X-ray density and internal strain as a function of dopant content of the as-synthesized samples is represented as shown in Fig. 3, and the estimated values are represented in Table 1.

Fig. 2 Variation of lattice parameter (Å) and crystallite size (nm) with Ce^{3+} content

Fig. 3 Variation of internal strain (%) and X-ray density (gm/cm^3) with Ce^{3+} content

3.1.2. SEM analysis of $\text{Co}_{0.5}\text{Ni}_{0.5}$ ferrites doped with Ce^{3+}

The SEM images of all the samples of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03) is depicted in Fig. 4. The corresponding EDS spectra of all the samples are shown in Fig. 5. The experimental elemental compositions of all the samples are summarized in Table 2. Experimental stoichiometry estimated from EDS data is in good agreement with that of the theoretical ones. The images are analyzed using Image J software; it reveals that the particles are grown with definite grain boundaries. It is clearly seen that particles are almost spherical and some aggregation is observed in all compositions. The average grain sizes of the samples are given in Table 1. The grain size distribution histogram of the nanoparticles for all the samples is shown in the inset of Fig. 4. As the Ce^{3+} content increases, the grain size is also increases. SEM micrographs reveal that the density of the samples increases with increase in Ce^{3+} content. This increase in density is a consequence of increase in Ce^{3+} concentration and simultaneous decrease in lattice parameter in the samples which enhances the grain growth and trumps the densification (Table 3).

3.2. Dielectric studies of $\text{Co}_{0.5}\text{Ni}_{0.5}$ ferrites doped with Ce^{3+}

The room-temperature frequency-dependent dispersions of dielectric constant of all the samples were investigated. Dielectric constant is a complex quantity which explores the response of material under the influence of an external alternating electric field. The real part (ε') is the quantity of energy stored from the electric field in the material and the imaginary part (ε'') is the quantity of the dissipation of energy in the system when subject to an alternating electric field.

The real part of dielectric constant is determined by using the following relation [22].

$$\varepsilon' = \frac{Ct}{A\varepsilon_0} \quad (5)$$

where C is the capacitance, t is the thickness of pellet, ε_0 is the permittivity of free space and A is the pellet area.

The effect of frequency of electric field on the real part of dielectric constant of Ce^{3+} substituted Co–Ni ferrite nanoparticles at room temperature is shown in Fig. 6. It reveals the dielectric constant decreased with increase in frequency and attains a constant value at high frequency for all the samples under investigation. The dielectric constant increases with increase in Ce^{3+} content in the samples. Dielectric constant dispersion with frequency is based on Maxwell–Wagner type of polarization phenomena [23].

Fig. 4 SEM images of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ ferrite nanoparticles, where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03 . The inset shows grain size distribution histogram

This is in good agreement with Koop's theory [24]. Higher value of dielectric constant at lower frequency is due to polarization effect arising from electronic, ionic, dipolar, and space charges. Polarization phenomena in ferrites took place due to the exchange of electrons between Fe^{2+} and Fe^{3+} ions on the octahedral sites which arising due to local displacement of electrons in the direction of applied electric field and these electrons brought the polarization. The extent of polarization becomes lower with increase in

frequency and attains a saturated value due to the fact that beyond a particular frequency of the applied external electric field the electron exchange does not follow the alternating field. Therefore, polarization was lagging behind the applied electric field at higher frequency. Substitution of larger ionic radii Ce^{3+} at the site of Fe^{3+} in the ferrite shows strong preferential occupancy at octahedral site which is evidenced from Rietveld refinement. With replacement of Fe^{3+} by Ce^{3+} migrates Fe^{3+} from

Fig. 5 SEM-EDS of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles; Where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03

octahedral site to tetrahedral, there is increase in dielectric constant with increase in Ce^{3+} content in the ferrite. Inclusion of Ce^{3+} distorts the Co–Ni lattice, which makes the increased $\text{Fe}^{3+}\text{--O}^{2-}$ and $\text{Ce}^{3+}\text{--O}^{2-}$ bond lengths in octahedral site results the increased polarization and hence increase in dielectric constant. It is found in the literature [25–27] that substitution of larger rare earth ion substitution into Cobalt ferrite or Nickel ferrite lattice shows the similar behavior of increase in resistivity and the dielectric constant with increase in dopant concentration [28–30]. For $x = 0.03$ composition of the sample the high value of dielectric constant is obtained in the present investigation.

Imaginary part of dielectric constant (ϵ'') is the measure of dissipation/loss of electrical energy in the ferrite sample. It can be estimated using the following relation [31].

$$\epsilon'' = \frac{\sigma}{\epsilon_0 \omega} \quad (6)$$

The trend of imaginary part of dielectric constant with applied frequency of alternating field is represented in Fig. 7. Dielectric behavior of the ferrite material can be understood based on the concept of polarization and hopping mechanism. The presence of Fe^{3+} and Fe^{2+} ions in the ferrite makes it as dipolar. The observed dielectric loss in the ferrite samples is attributed as follows. At lower frequencies the hopping of electron between Fe^{2+} and Fe^{3+} is predominant, as the frequency increases the hopping process get terminates because the hopping does not follow the frequency of applied field, i.e., if τ be the relaxation period of the dipoles, for low frequencies $f \ll (2\pi\tau)^{-1}$ the dipoles following the applied electric field, hence a larger

Table 2 Summary of SEM-EDS analysis of Co_{0.5}Ni_{0.5}Ce_xFe_{2-x}O₄ (where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03) ferrite nanoparticles

Ce ³⁺ content (x)	Element	Nominal composition	Experimental composition
0.0	Co	0.5	0.546
	Ni	0.5	0.454
	Ce	0.0	0
	Fe	2	2
0.01	Co	0.5	0.575
	Ni	0.5	0.425
	Ce	0.01	0.011
	Fe	1.99	1.989
0.015	Co	0.5	0.549
	Ni	0.5	0.451
	Ce	0.015	0.016
	Fe	1.985	1.984
0.02	Co	0.5	0.562
	Ni	0.5	0.437
	Ce	0.02	0.019
	Fe	1.98	1.981
0.025	Co	0.5	0.566
	Ni	0.5	0.434
	Ce	0.025	0.024
	Fe	1.975	1.976
0.03	Co	0.5	0.579
	Ni	0.5	0.421
	Ce	0.03	0.029
	Fe	1.97	1.971

value of ϵ'' . At high frequencies $f \gg (2\pi\tau)^{-1}$, the dipoles not at all follow the applied field, and therefore, ϵ'' values do not change appreciably.

Figure 8 depicts the variation of dielectric loss tangent ($\tan\delta$) with applied frequency at room temperature. Dielectric loss tangent of all the samples under investigation is calculated by using the relation [32].

Fig. 6 Variation of permittivity ϵ' (real part) with $\log f$ (Hz) of Co_{0.5}Ni_{0.5}Ce_xFe_{2-x}O₄ nanoparticles, where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03 **Fig. 7** Variation of permittivity ϵ'' (imaginary part) with $\log f$ (Hz) of Co_{0.5}Ni_{0.5}Ce_xFe_{2-x}O₄ nanoparticles, where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03 **Fig. 8** Variation of dielectric loss tangent ($\tan\delta$) with $\log f$ (Hz) of Co_{0.5}Ni_{0.5}Ce_xFe_{2-x}O₄ nanoparticles, where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03 **Table 3** Compositional dependence of room-temperature dielectric data of Co_{0.5}Ni_{0.5}Ce_xFe_{2-x}O₄ (where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03) ferrite nanoparticles

Sl. no.	Chemical formula	ϵ'	ϵ''	$\tan \delta$	σ_{AC} S/cm
1	Co _{0.5} Ni _{0.5} Fe ₂ O ₄	125.68	2510	19.9	1.4×10^{-9}
2	Co _{0.5} Ni _{0.5} Ce _{0.01} Fe _{1.99} O ₄	247.58	22896	79.8	1.27×10^{-8}
3	Co _{0.5} Ni _{0.5} Ce _{0.015} Fe _{1.985} O ₄	281.88	25093	81.2	1.39×10^{-8}
4	Co _{0.5} Ni _{0.5} Ce _{0.02} Fe _{1.98} O ₄	356.19	42540	101.35	2.36×10^{-8}
5	Co _{0.5} Ni _{0.5} Ce _{0.025} Fe _{1.975} O ₄	387.98	64518	109.64	3.58×10^{-8}
6	Co _{0.5} Ni _{0.5} Ce _{0.03} Fe _{1.97} O ₄	808.57	66247	186	3.68×10^{-8}

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (7)$$

The $\tan \delta$ values decreases with increase in frequency, it is a normal tendency of a ferrite material. The decrease in the values of $\tan \delta$ in the lower frequency region is very sharp, whereas at higher frequency, it is almost independent of frequency. This is attributed as follows, at lower frequency the high value of $\tan \delta$ is due to high resistivity of grain boundaries. To exchange electrons between Fe^{2+} and Fe^{3+} , the energy required is more and hence the loss is high. In the higher frequency region, the exchange of electrons is from low-resistivity grains [33], little energy is sufficient to electron transfer hence the loss is less. The nature of dielectric loss depends on many factors such as synthesis method, stoichiometry, dopant concentration and temperature. In our case, the dielectric loss tangent increases with increase in Ce^{3+} content. The composition with $x = 0.03$ having highest value of loss tangent. This is because addition of Ce^{3+} into the Co–Ni lattice makes the ferrite material to behave like a high-resistivity object.

3.3. Electrical studies of $\text{Co}_{0.5}\text{Ni}_{0.5}$ ferrites doped with Ce^{3+}

AC part of electrical conductivity of the ferrite samples were calculated using the following relation [34].

$$\sigma_{ac} = \epsilon' \epsilon_0 \omega \tan \delta \quad (8)$$

where ω is the angular frequency. Ac electrical conductivity as a function of frequency for all the ferrite samples is shown in Fig. 9. It reveals ac conductivity enhanced with the increase in frequency. This increasing trend is observed above the applied frequency 400 Hz. Before this, it almost exhibits the frequency-independent behavior. After 400 Hz, the increase in conductivity shows almost a linear variation with applied frequency.

In ferrites, the electrical conductivity is mainly due to hopping of electrons between ions of same element

existing in the different valence states. Ce^{3+} substitution at Fe^{3+} of B-site of a ferrite replaces the Fe^{3+} , there is a chance of Fe^{3+} occupancy at the A-site also. The hopping of electrons between A- and B-sites is most required as compared to A–A- and B–B-sites of the spinel ferrite. With the increase in Ce^{3+} concentration replaces more Fe^{3+} ions. Upon the application of ac field the electron hopping increases, thereby enhancing the ac conductivity. The charges migrating under the influence of applied ac field contributes to the electrical response of the system [35–37]. The ac conductivity can be represented by the following relation.

$$\sigma = \sigma_0(T) + \sigma_{ac}(\omega, T) \quad (9)$$

This equation is composed of two parts: First term is frequency-independent part called as dc conductivity which is due to band conduction, and the second frequency-dependent part is called as ac conductivity due to hopping of electrons at B-site. With the substitution of Ce^{3+} at Fe^{3+} site two distinct regions can be seen in Fig. 9. In the first region frequency up to 300 Hz, the conductivity curve is purely frequency independent designated as dc conductivity found to increase with Ce^{3+} concentration. In the second region, i.e., beyond 300 Hz at higher frequencies due to dielectric relaxation caused by the localized charge carriers, the conductivity curve starts increasing linearly and shifts toward higher conductivity with respect the Ce^{3+} doping concentration. The second term can be expressed as an empirical formula [38].

$$\sigma_{ac} = A\omega^n \quad (10)$$

where A constant having units of conductivity, ω is angular frequency and n is the slope of frequency-dependent region. This behavior follows Jonscher's power law. In the second region, the value of n increases from 0.442 to 0.774, and this increasing value of n suggests that the conductivity in the samples is due to the hopping of charges [39].

The impedance spectroscopic analysis is a significant technique to study the electrical properties of ferrite ceramics. Microstructure of the ferrite material is the most responsible factor which influences the impedance of the material. The variation of real part (Z') and imaginary part of impedance (Z'') of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ with ($x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03) with frequency at room temperature is shown in Figs. 10 and 11, respectively. The magnitude of Z' was found to be higher at lower frequency range. This behavior could be explained in terms of the enhanced hopping of charge carriers between the localized ions. The decrease in real part of the impedance at high frequency range can be attributed to the enhanced conductivity [40]. The imaginary part of impedance Z'' explains the reactance of capacitor. The imaginary part Z'' versus frequency plot shows an emergence of a broad peak

Fig. 9 Variation of $\log \sigma_{ac}$ with $\log f$ (Hz) of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles, where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03

Fig. 10 Variation of impedance Z' (real part) with $\log f$ (Hz) of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles, where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03

Fig. 11 Variation of impedance Z'' (imaginary part) with $\log f$ (Hz) of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticle, where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03

as shown in Fig. 11. From the figure, it can be observed that an occurrence of relaxation mechanism in the material. This relaxation mechanism decreases with the increase in Ce^{3+} content in the Co–Ni ferrites [41]. Complex impedance analysis is a significant technique to distinguish the transport characteristics occurring between the grains and grain boundaries and explains the change observed in the dielectric permittivity, dielectric losses, and conductivity of the material [42]. Impedance of material can be measured by series or parallel combination of RC equivalent circuit. Electrical properties of materials are also calculated in terms of complex Impedance (Z^*). Nyquist graph (variation of Z' with Z'') enunciates the impedance behavior of different ceramic samples and depicts different conduction and relaxation processes. The Nyquist plot of complex impedance of the synthesized Co–Ni ferrite doped with Ce^{3+} samples is shown in Fig. 12. The varying patterns of all the samples consist of semicircular arcs with their centers lying below the real axis. The centers of the semicircular arcs shift toward lower Z' values as the Ce^{3+} content increases in the ferrite samples simultaneously the radius of the semicircles also decreases. This indicates a non-Debye-type relaxation phenomenon in Co–Ni ferrites. The characteristic shapes of the curves shown in Fig. 12

provide interesting information such as giving an indication of existence of microstructural electrically active regions which are grain boundaries in the present investigation.

The dielectric data obtained at room temperature are further studied using complex modulus spectroscopic analysis. It is an important tool to analyze the relaxation phenomenon in electrically and ionically conducting materials and to determine the electrode polarizing effects which annihilate effectively [43]. The complex electric modulus is related to complex dielectric constant by the following relations.

$$M' = \frac{\epsilon'}{(\epsilon')^2 + (\epsilon'')^2} \quad (11)$$

$$M'' = \frac{\epsilon''}{(\epsilon')^2 + (\epsilon'')^2} \quad (12)$$

Here M' is the real part and M'' is the imaginary part of complex electric modulus. The trend of real part of modulus (M') with frequency is shown in Fig. 13. It is clear from the figure that the M' value increases with the increase in frequency. As the amount of rare earth Ce^{3+} ions in the cobalt nickel ferrite increases, the real part of modulus also increases with the increase in frequency. This is attributed due to the effect of space-charge polarization in the materials. The dispersion obtained in this plot corresponds to the short range mobility of the charge carriers. Figure 14 depicts the variation of M'' with frequency, which shows a broad peak for each sample indicating the existence of relaxation mechanism for Co–Ni ferrites. The shifting of peaks toward a lower frequency with the addition of Ce^{3+} contents shows the hopping of charge carriers at higher frequency [44–46]. This hopping was also responsible for high-frequency conduction mechanism. At lower frequencies, these charge carriers are confined to their potential wells [47].

The variation of real and imaginary part of electric modulus of cobalt–nickel ferrite with rare earth Ce^{3+} doped is shown in Fig. 15. It is clear from the figure that all samples show semicircles. The variation of the modulus M'' versus M' provides information about the conduction mechanism either is from grain or grain boundary exactly. The semicircles at higher frequencies represent the resistance of grain only and at small frequency represent the sum of resistance of grain and grain boundary [48–50]. It is observed from the figure that the main role in the conduction is due to grain boundary density. Addition of rare earth ions such as Ce^{3+} to the Co–Ni ferrites increases the grain boundary resistance.

Fig. 12 Cole–Cole plot of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ ferrite nanoparticles, where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03

Fig. 13 Variation of real part of electric modulus (M') with $\log f$ (Hz) of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles, where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03

Fig. 14 Variation of imaginary part of electric modulus (M'') with $\log f$ (Hz) of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles, where $x = 0.0, 0.01, 0.015, 0.02, 0.025$ and 0.03

Fig. 15 Complex electric modulus plots of $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ ferrite nanoparticles, where $x = 0.01, 0.015, 0.02, 0.025$ and 0.03

4. Conclusions

Larger rare earth Ce^{3+} substituted to Fe^{3+} site of $\text{Co}_{0.5}\text{Ni}_{0.5}$ ferrites are synthesized via modified solution combustion method using a mixture of fuels, glucose, and urea for the first time. XRD patterns confirm the formation of monophasic $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Ce}_x\text{Fe}_{2-x}\text{O}_4$ sample, the crystallite size is found in nanosize, the lattice parameter is decreasing with increase in Ce^{3+} content which is due to larger ionic radii of dopant replacing the smaller ionic radii Fe^{3+} leads to larger crystalline anisotropy and induced internal strain in the lattice. X-ray density increases because of larger mass of Ce^{3+} at Fe^{3+} site and decreases with lattice parameter. The densification of the material is observed with increase in Ce^{3+} concentration. SEM results confirm the synthesized particles are almost spherical and agglomerated. EDS analysis verifies the stoichiometry matches with the anticipated values without any impurity pickup. The behavior observed for real and imaginary part of dielectric constant, $\tan\delta$, for all ferrite compositions under investigation shows normal dielectric dispersion of ferrites with frequency. The dielectric parameters increase with increase in Ce^{3+} concentration and is maximum for $x = 0.03$ composition. The ac conductivity increases by doping of Ce^{3+} contents in the Co–Ni ferrites because the rare earth ions doped in the spinel ferrites affect the conduction mechanism. Impedance spectroscopy analysis confirms the existence of conduction mechanism in the ferrites and is mainly due to grain boundaries. Ferrite sample for $x = 0.03$ shows high dielectric constant desirable for high-frequency automotive device applications.

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