Dielectric, Electrical Transport and Magnetic Properties of Er³⁺ Substituted Nanocrystalline Cobalt Ferrite

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ABSTRACT

Erbium substituted cobalt ferrite ($\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$; $x=0.0-0.2$, referred to CFEO) materials were synthesized by sol-gel auto-combustion method. The effect of erbium (Er^{3+}) substitution on the crystal structure, dielectric, electrical transport and magnetic properties of cobalt ferrite is evaluated. $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics exhibit the spinel cubic structure without any impurity phase for $x \leq 0.10$ whereas formation of the ErFeO_3 orthoferrite secondary phase was observed for $x \geq 0.15$. All the CFEO samples demonstrate the typical hysteresis (M-H) behavior with a decrease in magnetization as a function of Er content due to weak superexchange interaction. The frequency (f) dependent dielectric constant (ϵ') revealed the usual dielectric dispersion. The $\epsilon'-f$ dispersion ($f=20\text{Hz} - 1\text{MHz}$) fits to the modified Debye's function with more than one ion contributing to the relaxation. The relaxation time and spread factor derived are $\sim 10^{-4}$ s and $\sim 0.61(\pm 0.04)$, respectively. Electrical and dielectric studies indicate that ϵ' increases and the dc electrical resistivity decreases as a function of Er content ($x \leq 0.15$). Complex impedance analyses confirm only the grain interior contribution to the conduction process. Temperature dependent electrical transport and room temperature ac conductivity (σ_{ac}) analyses indicate the semiconducting nature and small polaron hopping.

Keywords: Cobalt ferrite; sol-gel auto-combustion; dielectric response; electrical transport; magnetic properties

1. Introduction

Ferrites, which are a class of ‘magnetic materials,’ have been the attention of researchers for several decades due to their remarkable applications in high density magnetic recording, magnetic fluids, spintronics, biotechnology, high frequency data storage and gas sensors [1-3]. Cobalt ferrite (CoFe_2O_4 ; CFO), which is the most versatile hard ferrimagnetic material, exhibits unique properties such as high Curie temperature (520°C), high coercivity (5400 Oe), high magneto-crystalline anisotropy, moderate saturation magnetization (80 emu/g) at 300 K , large Kerr effect and Faraday rotation [4-7]. CFO materials are also utilized in high frequency and power devices especially for electromagnetic interference suppression (EMIS), phase shifters and circulators for mobile phones [8]. In addition, CFO finds application in lithium (Li) batteries and super capacitors [9]. However, the physical, structural, electrical, magnetic and dielectric properties of CFO are sensitive to the method of synthesis, reactive/processing atmosphere, size and morphology of the particles and cation doping in the host crystal structure that substitute for $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions [9-11]. On the other hand, for electrical and electro-magnetic applications, electrical transport, impedance and dielectric properties are quite important [5-13].

The present work was performed on erbium (Er^{3+}) substituted CFO. The objective is to understand the Er-substitution induced effects on the structural, electrical transport, impedance and dielectric properties of CFO. For the purpose, well established sol-gel auto-combustion technique was adopted for synthesis in view its demonstrated suitability for the synthesis of nanocrystalline oxides/ferrites with homogeneous microstructure, narrow size distribution and uniform shape at lower processing temperatures. The reason for undertaking the detailed investigation of Er-substitution is as follows. It is well known that rare earth (RE) ions have unpaired $4f$ electrons and the strong spin-orbit coupling therefore substitution of RE ions into spinel ferrite, leads to the presence of $4f-3d$ couplings, which can also modify the electrical and

magnetic properties of spinel ferrites. Rare-earth ion substitution is, therefore, becoming a promising way of improving the dielectric and electromagnetic properties and EMI shielding effectiveness of ferrites [14]. In modern technology, most of the electronic gadgets are wireless with higher chip speed indicates the need against the penetration of the radiation through the shield [15]. For significant absorption of the radiation by the shield, the shield should have electric and/or magnetic dipoles, which interact with the electromagnetic field in the radiation. For electric dipoles, the dielectric constant should be sufficiently high. As such, while the magnetic dipoles are readily present due to the ferromagnetic nature of the cobalt ferrite, enhanced dielectric constant is expected due to the rare earth (Er^{3+}) substitution at the Fe site in the cobalt ferrite. Furthermore, the mechanism of multiple reflections at various surfaces or interfaces in the shield requires a larger surface in the shield [16]. This requirement can be fulfilled by the nanocrystalline materials, which offer exceedingly higher surface-to-volume ratio. Thus, Er substitution coupled with morphology-controlled CFO is expected to offer the possible candidate materials for the shielding applications.

The substitution of RE ions for Fe in Co ferrite leads to the structural disorder and lattice strain [9], which allows tuning the dielectric and electrical properties [11, 18]. The overall electrical and magnetic properties of ferrites depend upon the nature of ions, their oxidation states, and their distribution among the tetrahedral and octahedral (B) sites [14]. Er^{3+} is nonmagnetic at room temperature; however, Er^{3+} substitution for Fe^{3+} in CFO induces significant saturation magnetization, which is extremely useful to tailor the properties and performance [14]. **Furthermore**, in connection with the variation of f -shell electron orbital contribution to the magnetic interactions, Er^{3+} can be either isotropic or anisotropic. Therefore, introducing the trivalent rare earth (RE) cations such as Er^{3+} into the inverse spinel ferrite lattice will also induce

RE³⁺-Fe³⁺ interactions, which could modify the corresponding magnetic properties [6,19-21]. As such, a better understanding of the dielectric and transport properties of Er substituted CFO ceramics may be useful to fabricate materials for electromagnetic applications. Furthermore, while the overall attention paid towards Er³⁺ substitution in CFO is meager, there is some controversy related with the composition and crystal structure as a function of Er content [6, 19, 22-23]. Therefore, the present work on the dielectric and electrical transport properties along with complex impedance spectroscopic analyses of the Er-substituted CFO is expected to further contribute to the current understanding of the RE ion incorporation effects in ferrites.

2. Materials and methods

2.1. Synthesis

Nanocrystalline CoFe_{2-x}Er_xO₄ (CFEO; $x=0.0-0.2$) ceramics were synthesized by citrate-nitrate sol-gel auto combustion route, which is advantageous over other conventional methods. For the synthesis of CFEO composition, the analytical reagent (AR) grade nitrates of Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, Er(NO₃)₃·6H₂O and citric acid (C₆H₈O₇·H₂O) were used as raw precursors. Stoichiometric amount of metal nitrates and citric acid with 1:1 ratio were dissolved in deionized water to form citrate-nitrate solution then the liquor ammonia was added drop by drop into the citrate-nitrate solution to adjust the pH (≈ 7). The final solution was continuously stirred on a magnetic stirrer to homogenize the solution and to form the redox mixture of citric acid and metal nitrates for combustion reaction. Then the resultant solution was dehydrated slowly on a hot plate at 80 °C with continuous stirring until the viscous xerogel was formed. On further heating, the temperature of gel increased and at a certain temperature auto-ignition of the gel took place with evolution of gases and the black powder was obtained. To determine the processing temperatures, thermo gravimetric-differential thermal analysis (TG-

DTA) was performed on the black powder samples. By considering the results of TG-DTA analysis (not shown here), the samples were finally sintered at 700 °C for 5 hr.

2.2. Characterization

Crystal structure of the ceramics was examined using the X-ray diffraction (XRD) unit with CuK_α radiation ($\lambda=1.54178 \text{ \AA}$; D8 Advance, Bruker Inc., Karlsruhe, Germany). Electrical and dielectric measurements were made on the pelletized samples. The magnetic properties of all the samples were investigated at 300 K, using a Vibrating sample magnetometer with a model, Lakeshore-7307. To ensure better Ohmic contact, prior to transport property measurements, the silver paste was painted on to the polished surfaces of the pellet and cured at 100 °C for 3hr. The frequency dependence of dielectric permittivity (ϵ') and dissipation factor ($\tan \delta$) in the range from 20 Hz to 1 MHz were studied using a precision LCR meter bridge (HP 4284 A). AC conductivities were calculated using room-temperature dielectric data. The impedance parameters, namely Z' and Z'' for all the samples, were measured at room temperature in the frequency range from 20 Hz to 1 MHz using a precision LCR meter bridge (HP4284 A). The *dc* resistivity measurements were carried out using two-probe method in the temperature range from room temperature to 500 °C.

3. Results and discussion

3.1. Crystal structure and morphology

The XRD patterns obtained for $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ($x=0.0-0.2$) are shown in Fig. 1. Er-substituted CFO exhibit all the characteristic reflections expected for ferrites. Most intense is the (311) reflection. The XRD data, thus, confirms the formation of a cubic spinel structure, space group $Fd3m$ (227). It is evident that the ceramics with lower Er content ($x \leq 0.10$) corresponds to the single phase cubic spinel structure without any other peaks corresponding to impurity or

secondary phase. The XRD results were analyzed using JCPDS cards: 22-1086 (CoFe_2O_4) and 47-0072 (ErFeO_3). However, the $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics with higher Er content ($x \geq 0.15$) exhibit smaller amount of ErFeO_3 orthoferrite in addition to the primary spinel ferrite phase. As widely reported in the literature, doping of rare earth (RE) into the spinel lattice suffers the phase segregation and diffusion to the grain boundaries even for very low concentrations, causing the precipitation of extra amorphous or crystalline phases such as orthoferrite (REFeO_3), hematite ($\alpha\text{-Fe}_2\text{O}_3$), and metal monoxides [6-7, 25]. Therefore, in the context of RE-substituted ferrites, Er-substituted CFO without any impurity phase ($x \leq 0.10$) is remarkable which is due to the advantage of auto-combustion method.

Erbium substitution induced effects on the structure are reflected in two important observations: (1) slight increase in lattice constant and (2) decrease in crystallite size. The lattice constant calculated from XRD increases slightly from 8.38 Å ($x=0.0$) to 8.40 Å ($x=0.2$) obeying Vegard's law [26]. The crystallite size, L , of CFEO samples was calculated from the XRD pattern using the well-known Scherrer formula [27]:

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

where, λ is the X-ray wavelength in nanometer (nm), β is the peak width (in radians) of the diffraction peak profile at half maximum height resulting from small crystallite size and K is a constant related to crystallite shape, normally taken as 0.9. The intense (311) peak data were used for the size (L) estimate. The result shows the decrease in crystallite size from 43.59 (± 0.5) nm ($x=0.0$) to 21.5 (± 0.5) nm ($x=0.2$). Furthermore, the highly intense (311) peak is noted to shift towards the lower angle (Fig. 2) with increasing x -values. The physical parameters calculated from XRD are presented in Table 1. The lattice constant increase may be attributed to the

replacement of smaller Co^{2+} (0.78 Å) and Fe^{3+} (0.64 Å) ions by the larger Er^{3+} (0.90 Å) ions in Co-Fe-Er spinel lattice. Thus, due to the larger differences in the ionic radii of Co^{2+} - Fe^{3+} - Er^{3+} ions, strain is induced during diffusion as well as lattice formation due to larger Er^{3+} ion [6,11,17,19,28]. Since a large amount of energy is required to incorporate the RE^{3+} ions with larger ionic radii in place of Fe^{3+} and to form the RE-O bond, the energy supplied is utilized for this process at the expense of crystallization and hence the decrease in crystallinity with smaller particle size is observed. Similar results are reported for RE-ion substituted cobalt ferrite in the literature [26, 28, 29-30]. The energy dispersive X-ray spectrometry (EDS) confirm (shown in Table 1) the effective Er-incorporation into CFO and stoichiometric amount of Co, Fe, Er and O atoms. Thus, the observed XRD results account for the unit cell expansion due to the larger Er^{3+} ion substitution in CFO. The X-ray density (D_x) was also calculated using:

$$D_x = \frac{8M}{Na^3} \quad (2)$$

where, M is the molecular weight of ferrite composition, N is the Avogadro's number ($6.023 \times 10^{23} \text{ mol}^{-1}$) and ' a ' is the lattice constant. The calculated X-ray density increases from 5.29 gm/cm^3 (for $x = 0.00$) to 5.75 gm/cm^3 (for $x = 0.20$) with Er^{3+} content in CFO.

3.2. Dielectric properties

The variation of ϵ' with frequency at room temperature for the $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ($x=0.0-0.2$) samples is shown in Fig. 3. ϵ' initially decreases sharply with increasing frequency (up to 1 kHz) and then decreases slowly at higher frequency (>1 kHz) and remains constant (up to 1 MHz). Thus, the usual dielectric dispersion expected for ferrites is noted for all the $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ($x=0.0-0.2$) ceramics but with a marked difference in the ϵ' -magnitude due to Er-content. The larger value of ϵ' at lower frequencies is mainly due to the contributions from ionic polarizations.

At higher frequencies, ε' remains independent of frequency due to the inability of electric dipoles to follow the fast variation of alternating applied electric field [31-32]. The experimental data were fitted to the modified Debye's function that considers the possibility of more than one ion (O^{2-} , Fe^{3+} , Co^{2+} , and Er^{3+} ions) contributing to the relaxation [5-6]. Using this model, the observed dispersion of dielectric constant can be modeled using the equation

$$\varepsilon' = \varepsilon_{\infty}' + \frac{(\varepsilon_0' - \varepsilon_{\infty}')}{[1 + (\omega\tau)^2(1-\alpha)]} \quad (3)$$

where ε' is the real part of dielectric constant, ε_{∞}' is the dielectric constant at higher frequency (at 1 MHz), ε_0' is the dielectric constant at lowest possible frequency (20 Hz), $\omega=2\pi f$ is the angular frequency with f is the applied frequency to the signal of 1 V, τ is the mean relaxation time, and α is the spread factor of the actual relaxation times about the mean value. The pioneering work of Cole-Cole and the standard procedure was adopted in this work to fit the data and to obtain α value for CFEO materials [5-6, 33]. The real part of dielectric constant instead of complex part of dielectric constant is considered to plot $\ln[(\varepsilon_0' - \varepsilon')/(\varepsilon' - \varepsilon_{\infty}')] versus \ln(\omega)$ (Fig. 4) for all the Er-compositions (x). The data obtained for CFEO ceramics yield straight line (Fig.4). The parameter $(1-\alpha)$ is determined from the slope of the linear plot which, in turn, provides the value of spread factor ' α .' The calculated values of α and τ for $CoFe_{2-x}Er_xO_4$ ($x=0.0-0.2$) ceramics are listed in Table 2. Using τ and α , the experimentally measured ε' is fitted with the model, Eq. (3), as presented in Fig. 3. It is observed that the experimental data is in good agreement with the calculated data indicating the validity of modified Debye's function with the possibility of more than one ion contributing to the relaxation process in $CoFe_{2-x}Er_xO_4$ ($x=0.0-0.2$) nanocrystalline ceramics.

The origin behind Er-substitution induced the improvement in dielectric properties can be understood as follows. The increase in ϵ' from 125 to 350 can be attributed to the decrease in resistivity of CFO (as discussed under dc resistivity studies) since the dielectric permittivity is directly proportional to the square root of conductivity [34]. Another possible reason for the ϵ' -increase with Er-concentration is the particle/grain size reduction as evidenced from XRD and SEM data. In fact, for CFO, ϵ' enhancement due to size reduction has been reported several times [14, 26, 29-30]. In addition, lower Fe^{2+} ion concentration at B-site may also be responsible to have the low value of resistivity and hence a high value of ϵ' [11,12]. However, in the present case of $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics, observed ϵ' decrease for the higher Er-content ($x=0.2$) may be due to the formation of ErFeO_3 impurity phase, which increases the resistivity again. Note that the resistivity of a material increases as a result of imperfections, such as defects, impurities, grain boundaries, and dislocations [6, 19, 35-36]. Thus, ErFeO_3 phase formation as noted in XRD for higher Er-content may be considered as a defect phase contributing to the overall ϵ' decrease.

3.3. Impedance spectroscopic analysis

The complex impedance data of $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics measured at room temperature are shown in Fig. 5. The Nyquist plot exhibits the presence of a single semicircular arc for all the $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics in the frequency range of 20 Hz – 1MHz. The diameter of the semicircle corresponds to the resistance of the grain [6, 14]. It can be seen that the diameter of the semicircle decreases as the Er content increases indicating a decrease in the grain-resistance [6,35]. This may be due to the increase in frequency of an applied field; the conductive grains become more active thereby promoting the hopping between Fe^{2+} and Fe^{3+} ions. This may also be attributed to the Er-induced grain-size reduction, which makes grains more conductive [6,34].

To analyze the experimental impedance spectra, usually data are modeled by an ideal equivalent circuit consisting of a resistor R and a capacitor C [6,35]. The observed semicircle can be modelled by an equivalent circuit consisting of a parallel combination of grain resistance (R_g) and grain capacitance (C_g) (Fig. 5, inset). This RC equivalent circuit accurately simulates each Cole-Cole semicircle. In the analysis, the complex impedance is represented by:

$$Z = Z' - jZ'' \quad (4)$$

where,

$$Z' = \frac{R_g}{1 + R_g^2 \omega^2 C_g^2} \quad (5)$$

$$Z'' = \frac{R_g^2 \omega C_g}{1 + R_g^2 \omega^2 C_g^2} \quad (6)$$

The observed and calculated complex impedance data are in good agreement with each other (Fig. 5). C_g and R_g values obtained from the best fitting are listed in Table 2. R_g decreases with increasing Er content. It should be noted that the grain capacitance, C_g , strongly depends on Er content and becomes maximum (83 pF) for $x=0.15$ and then decreases for $x=0.20$ (68 pF). These observations confirm that the increasing dielectric constant of CFEO is associated with an intrinsic feature, such as the grain capacitance (C_g). In the present case, the low-frequency semicircle, which contributes the grain boundary effect is absent at room temperature due to nanocrystalline grain size.

3.4. AC Conductivity (σ_{ac})

From the dielectric loss and dielectric permittivity of ferrites, σ_{ac} can be evaluated using the relation [32]:

$$\sigma_{ac} = 2\pi\epsilon_0 \epsilon' f \tan\delta \quad (7)$$

where f is the frequency of the applied field, ϵ_0 is the permittivity of free space, ϵ' is the real part of dielectric constant of the samples, $\tan \delta$ is the loss factor and σ_{ac} is ac conductivity [6,32]. The

ac conductivity data of CFEO ceramics are presented in Fig. 6. The plots are linear indicating the small polaron type conduction [12,32] present in the $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics. Furthermore, in case of large polaron hopping, the ac conductivity decreases with frequency, whereas in small polaron hopping it increases with frequency [32]. In the present case, the plots for ac conductivity measurement are almost linear, validating that the conduction is due to small polaron hopping [32, 35]. This linear increase in ac conductivity corresponds to the electron exchange between the ions of same element but difference valence states. This electron exchange increases under the application of AC field resulting an increase in ac conductivity [13,32]. In addition, as the frequency of applied field increases, the conductive grains become more active in promoting electron hopping between two adjacent octahedral (B-sites) sites and a transition between Fe^{2+} and Fe^{3+} ions. This in turn increases the rate of hopping conduction resulting in a gradual increase in the conductivity with frequency [6, 14, 29].

3.5. DC Resistivity (ρ_{dc}):

The temperature dependence of dc electrical resistivity (ρ_{dc}) for $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics is shown in Fig. 7. ρ_{dc} decreases exponentially with increasing temperature indicating the semiconducting nature of $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics. Thermally activated drift mobility of charge carriers in the hopping conduction mechanism is accounted for the observed behavior. As the electrical resistivity changes with the cation distribution in ferrites, the electron hopping between Fe^{2+} and Fe^{3+} and hole hopping between Co^{3+} to Co^{2+} ions at B site decides ρ_{dc} of $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics. It is found that ρ_{dc} decreases initially with Er^{3+} content ($x \leq 0.15$). While a more detailed account of deeper chemical characterization is not made on these samples, the trend observed can be due to the fact that when the iron is substituted by Er^{3+} , a part of Er^{3+} will occupy the octahedral sites displacing Co^{2+} from octahedral (B) site to tetrahedral (A) site i.e. (B to A) which is accompanied by an opposite transfer of an equivalent number of Fe^{3+} ions from A to B

sites in order to relax the strain [6,18]. This increase in Fe^{3+} ions in the octahedral sites will increase the number of Fe^{2+} and Fe^{3+} pairs in octahedral sites which in turn increases the conductivity. Therefore, ρ_{dc} decreases initially with Er substitution. However, further increase in Er content ($x=0.20$), slightly increases ρ_{dc} . Increasing concentration of Er ions at B-site increases the separation between Fe^{3+} to Fe^{2+} ions in proportion with their ionic radius. It hinders the electron transfer between Fe^{3+} and Fe^{2+} ions. Accordingly, ρ_{dc} increases slightly for higher Er content.

The mobility of a large polaron is often limited (at least in certain temperature ranges) by scattering due to (real) optical phonons, as a result of the strong electron-optical-phonon coupling in these materials. However, the transport of small polarons is generally via thermally-activated hopping [37]. As distinct from large polarons, small polarons appear due to short-range forces, and is reflected in the magnitude of activation energy [38]. **Parker et al.** have reported that the characteristic activation energy values for small polaron hopping are in the range of 0.15-0.30 eV [32]. The activation energy values of CFEO materials are calculated using the temperature dependent change in resistivity as given by Arrhenius equation:

$$\rho = \rho_0 \times \exp\left(\frac{\Delta E}{kT}\right) \quad (8)$$

where ΔE is the activation energy and k is the Boltzmann constant. The activation energy values determined from the slope of $\log \rho$ versus $1000/T$ plots (Fig. 7) are presented in Table 2. A wide range of activation energy values are reported in the literature for intrinsic and ion-doped/substituted ferrites. The low end of activation energies obtained in this work for Er^{3+} ion substituted cobalt ferrite may be due to the fact that the charge transport is in the nano-sized grains of CFEO [6]. The increased values of activation energies with Er content suggest that more energy is required to promote charge transport in CFEO which is a direct consequence of

larger Er^{3+} ion incorporation into the CFO lattice [6-7,33]. Most notable feature is that, in the present case of CFEO, the magnitude of activation energies are within this range (0.20-0.25 eV), which further authenticate that the conduction mechanism in these materials is due to the small polaron hopping [6, 39].

3.5. Magnetic properties

The room temperature (300 K) magnetization (M-H) data of $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ($x=0.00-0.20$) are shown in Figure 8. It is seen that all the samples exhibit the typical hysteresis behavior of long range ferrimagnetic ordering with a decrease in magnetization as a function of Er content, which is well supported by Neel's sublattice model for ferrites. It is well known that the $4f$ electrons of rare earth ions are generally remains to be highly localized in a solid and form the magnetic electrons unlike the corresponding $3d$ transition series elements. As the erbium shows the magnetic ordering at low temperature (88 K) [17], it may not have contribution to the magnetization at room temperature. Therefore, in the present study, it is assumed that Er^{3+} ions are nonmagnetic at room temperature. Furthermore, the decrease in magnetization (μ_B) with Er^{3+} substitution may be explained by a combination of more lattice defects and weaker magnetic superexchange interactions between A and B sites in ferrites [22]. In addition, as Er^{3+} ions replace Fe^{3+} at B site results in a decrease of strong $\text{Fe}^{3+}\text{-Fe}^{3+}$ negative interaction, thus reducing the net magnetization [40]. Similarly, the observed decreasing magnetic moment behavior with Er^{3+} substitution is well supported by the existing Neel's sub lattice model for ferrites; according to the theory, the two sub lattice model of ferrimagnetism, the net magnetic moment ($\sim\mu_B$) is expressed as [22,40]

$$\mu_B = M_B - M_A = 3 + 5(1-x) - 5 = 3 - 5x \quad (9)$$

where M_B and M_A are the B and A sub lattice magnetic moments, respectively. The magnitude of magnetic moment obtained from experimental data at 300 K and calculated from Neel's theory is in good agreement with each other as presented in Table 2. The magnetic moment decreases as Er content increases. This decrease in net magnetic moment can also be due to the migration of small amount of Co^{2+} ($3d^7$) ions from the octahedral to the tetrahedral sites with a magnetic moment aligned anti-parallel to those present at B site in the spinel lattice. At the higher Er^{3+} content ($x \geq 0.15$), the presence of antiferromagnetic orthoferrite (ErFeO_3) phase is expected to initiate the pinning of domain walls of the ferrimagnetic phase along with the existing ferrimagnetic phase and this may also leads to decrease in magnetization [35]. It is well known that the coercive field (H_c) in pure CFO is predominantly due to the single ion anisotropy of the octahedral Co^{2+} [19]. Similar to Co^{2+} , the rare earths generally have a strong L-S coupling and thereby contribute to the anisotropy of RE- substituted CFO when they are located in octahedral site [19]. The initial increase in coercivity H_c for CFEO ($x = 0.05$) is consequently due to the increase in anisotropy with Er^{3+} substitution. With further increase in Er content, the coercivity follows the similar trend of anisotropy constant and is shown in Fig. 9. Furthermore, the domain wall motion of a ferrimagnetic phase through an antiferromagnetic phase is generally complex [17] and in the present case this mechanism probably works together to decrease H_c .

4. Conclusions

The Er-induced effect on the crystal structure, morphology, dielectric constant and electrical transport properties of cobalt ferrite ceramics is significant. Traces of secondary ErFeO_3 along with primary spinel cubic structure occurs only for higher Er-content, $x \geq 0.15$. Magnetic properties are observed to be strongly dependent on Er substitution and the variation in coercivity is in accordance with the change in anisotropy constant. The Er-substitution enhances

the dielectric constant which is a combined effect of resistivity decrease and site-specific electric charge exchange. The dispersion of dielectric constant follows the modified Debye's function with more than one ion contributing to the dielectric relaxation. Complex impedance analysis confirms the grain-interior contribution in the conduction process in Er-substituted cobalt ferrites. Small polaron hopping and thermal activation of charge carrier mobility are operative in CFEO ceramics as evident in AC and DC electrical measurements. The presence of magnetic dipole along with increased dielectric constant could be useful for considering the Er-substituted cobalt ferrites for electronic and electromagnetic applications.

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Figure Captions

Figure 1. XRD patterns for $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics. The data shown are for variable Er content (x).

Figure 2. Magnified view of the (311) peak for $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics. Shift in the peak position is evident.

Figure 3. Dielectric constant (ϵ') as a function of frequency for $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ferrites at room temperature. The data are fitted with the modified Debye model taking the spreading factor (α) determined from Cole-Cole method (Fig. 5) into account. The observed and calculated data are in good agreement indicating the applicability of Debye model with more than one ion contributing to the relaxation (see, text).

Figure 4. $\ln[(\epsilon'_0 - \epsilon')/(\epsilon' - \epsilon'_\infty)]$ Vs $\ln\omega$ plots for $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics.

Figure 5. Complex impedance spectroscopic (Nyquist) plots of $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ ceramics. The experimental and calculated data are shown. A reasonable good agreement between observed and calculated data can be seen. The equivalent R, C circuit to calculate the spectra are shown in inset.

Figure 6. Variation of ac conductivity with frequency for $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$.

Figure 7. Variation of DC resistivity ($\log\rho$) with temperature ($1000/T$) for $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$.

Figure 8. Magnetic hysteresis loops for $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$ at 300 K

Figure 9. Variation of coercive field and anisotropy constant with Er content for $\text{CoFe}_{2-x}\text{Er}_x\text{O}_4$.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1: The physical parameters of CFEO ceramics determined from XRD, SEM, EDX analysis

Er content (<i>x</i>)	Crystallite size (XRD- nm)	Grain size (SEM-nm)	EDX Analysis (Atomic %)			
			Co	Fe	Er	O
0.00	43.59	120	13.30	26.53	0.00	60.17
0.05	27.82	85	11.48	25.68	0.84	62.00
0.10	25.44	54	11.39	25.02	1.48	62.11
0.15	24.36	42	10.61	23.63	2.25	63.51
0.20	21.50	32	10.50	22.71	2.97	63.82

Table 2: The **magnetic and** electrical parameters of CFEO ceramics determined from magnetic, dielectric, complex impedance and dc electrical resistivity measurements.

Er content (<i>x</i>)	Ms (Obs.) (emu/gm)	Ms (Obs.) (μ_B)	Ms (Neel's The.) (μ_B)	α	τ $\times 10^{-4}$ s	R_g ($M\Omega$)	C_g (pF)	E_g (eV)
0.00	66.41	2.79	3.00	0.6414	9.8511	6.350	64.5	0.2182
0.05	60.69	2.61	2.75	0.5917	9.5630	1.300	73.0	0.2236
0.10	56.59	2.49	2.5	0.6342	8.5672	0.945	79.0	0.2283
0.15	52.39	2.41	2.25	0.5833	9.5914	0.730	83.0	0.2386
0.20	47.78	2.15	2.00	0.5914	9.6743	1.150	68.0	0.2317