High temperature thermal cycling effect on the irreversible responses of lattice structure, magnetic properties and electrical conductivity in \( \text{Co}_{2.75}\text{Fe}_{0.25}\text{O}_{4+\delta} \) spinel oxide

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**Abstract:** We report high temperature synchrotron X-ray diffraction (SXRD), dc magnetization and current-voltage (I-V) characteristics for the samples of \( \text{Co}_{2.75}\text{Fe}_{0.25}\text{O}_4 \) ferrite. The material was prepared by chemical reaction of the Fe and Co nitrate solutions at pH ~ 11 and subsequent annealing at temperatures 200 °C, 500 °C and 900 °C. The measurements were performed by cycling the temperature from 300 K to high temperature (warming mode) and return back to 300 K (cooling mode). The SXRD patterns indicated a fine bi-phased cubic spinel structure in the highly Co rich spinel oxide. Magnetization curves showed intrinsic ferrimagnetic features and defect induced additional ferromagnetic phase at higher temperatures. Electrical conductivity showed thermal hysteresis loop between warming and cooling modes of temperature variation. The samples exhibited new information on the irreversibility phenomena of lattice structure, magnetization and electrical conductivity on cycling the measurement temperatures.

**Key words:** Co rich spinel oxide; Synchrotron X-ray diffraction; Bi-phased magnetic material; thermal dependent irreversible properties.
1. INTRODUCTION

The spinel oxides belong to an important class of strongly spin correlated electronic system. They are defined by formula unit $AB_2O_4$, where the metal ions (cations) occupy two inequivalent lattice sites A and B with tetrahedrally coordinated nearest neighbor oxygen ions (anions) and octahedrally coordinated oxygen ions, respectively in the cubic crystal lattice with space group $Fd\bar{3}m$ [1, 2]. The spinel oxides constitute in the phase diagram of Fe$_3$O$_4$ (magnetite) and Co$_3$O$_4$ (cobaltite) have exhibited a rich variety of magnetic and electronic properties. Among them, Co rich ferrites (Fe$_{3-x}$Co$_x$O$_4$; $1 < x < 3$) are attractive due to their ability for tuning physical properties by altering synthesis route, heat treatment, and Co content in cubic spinel structure [3-13]. The distribution of Co and Fe ions in A and B sites, and charge state of the cations determine magnetic and electrical properties in cubic spinel structure. Structural phase of the Co rich spinels that lie in the miscibility gap of Fe$_3$O$_4$-Co$_3$O$_4$ phase diagram is thermodynamically sensitive to Co content and thermal annealing [1]. The thermal annealing in the temperature range 900–950°C shows structurally stable phase. Otherwise, cubic spinel phase shows spinodal decomposition into Co- and Fe-rich phases. Such self-composite materials are characteristically different from hybrid composites [14]. Recently, thin films of Co$_{1.8}$Fe$_{1.2}$O$_4$ (Co rich and Fe rich phases) [15] and Mn ferrite (Mn rich and Fe rich phases) [16] showed spinodal decomposition. Additional phases ($\alpha$-Fe$_2$O$_3$ and CoO) also appeared during spinodal decomposition of Co rich spinel ferrites [17, 18]. The modification of structural phase affects to physical properties.

High temperature study provided a better insight of the structure-property relationship in spinel oxides. Balagurov et al. [19] reported a correlation between structure and magnetic phase of CuFe$_2$O$_4$ using neutron diffraction patterns in the temperature range 2-820 K. It shows a fully inverted tetragonal spinel phase up to temperature till a cubic phase appeared at 660 K. Both
phases coexisted up to 700 K and cubic phase alone stabilized at higher temperatures. The ferrimagnetic structure disappeared at $T_N \sim 750$ K. The correlation between structure and magnetic properties showed composition dependent in Mn$_x$Fe$_{3-x}$O$_4$, which at room temperature crystallizes in cubic phase for $x < 2$ and tetragonal phase for $x \geq 2$ [20]. Nepal et al. [21] reported a structural phase transition at $\sim 595$ K from (low temperature) tetragonal phase to (high temperature) cubic phase with two ferrimagnetic transitions at $\sim 373$ K and $\sim 50$ K for FeMn$_2$O$_4$. O’Neill et al. [22] performed neutron diffraction experiments in the temperature range 300 K-1700 K to study thermal cycling effect on cation order-disorder process in Mg$_2$TiO$_4$. The distribution of Mg$^{2+}$ and Ti$^{4+}$ ions was found to be in ordered state (inverse structure with all Ti$^{4+}$ ions occupy half of the B sites) when sample temperature was warmed from 300 K to 1173 K and a disordered state (migration of a fraction of Ti$^{4+}$ to A sites) appeared at higher temperatures. The rate of reordering of the cations between A and B sites observed fast during cooling process, and the high-temperature disordered state was not preserved on cooling back the sample to room temperature. Antao et al. [23] carried out high temperature (300-1250 K) synchrotron XRD experiments on MgFe$_2$O$_4$ spinel oxide. The variation of unit-cell parameter during thermal cyclic process (warming followed by cooling) was correlated to the distribution of cations among A and B sites. Apart from thermal cycling induced perturbation of the ordered state of cations from their equilibrium trajectories, intrinsic point defects in cubic spinel structure played an important role in modifying the high temperature magnetic and electrical properties [24-26].

Based on above cited works, the high temperature properties of Co rich spinel ferrite are expected to be different from their low temperature regime (5K-400 K) [5, 8, 27]. Such magnetic material with spatially inhomogeneous lattice, magnetic spin order and electronic structure are useful for studying first order magnetic phase transition and also for achieving high magneto-
caloric effect [28-30]. In this work, we report the high temperature properties of lattice structure, magnetism and electrical conductivity for $\text{Co}_{2.75}\text{Fe}_{0.25}\text{O}_4$, whose composition is close to the AFM normal spinel oxide $\text{Co}_3\text{O}_4$ with a small replacement of Co by Fe. We highlight the role of irreversibility effects on the structure, magnetic phase and electrical conductivity during measurement temperature cycling (300 K to high temperature and back to 300 K). The measurements were carried out in air to understand the effects of naturally created defects in spinel structure during high temperature measurements.

2. EXPERIMENTAL

A. Sample preparation

The spinel oxide $\text{Co}_{2.75}\text{Fe}_{0.25}\text{O}_4$ was prepared through chemical reaction of the required amounts of $\text{Co(NO}_3)_2$.6$H_2$O and $\text{Fe(NO}_3)_3$.9$H_2$O salts. The salts were dissolved in distilled water to yield a transparent aqueous solution at pH $\sim$ 1.4. Sodium hydroxide (NaOH) solution with initial pH $\sim$ 13 was used as the precipitating agent and added gradually into the nitrate solution until the pH reached to $\sim$ 11. The reaction temperature was maintained at 80 °C for 4 h with continuous magnetic stirring. The pH was maintained at 11 by adding required amount of NaOH solution during heating at 80 °C. The products were allowed to cool down to room temperature and allowed to precipitate at the bottom of a Borosil beaker. The transparent solution from the top portion was removed carefully and remaining product was washed several times with distilled water and each time it was dried at 100 °C. Finally, the resultant powder was heated at 200-250 °C in a beaker to confirm the complete removal of the bi-product of NaNO$_3$, which formed a white coating on the wall of beaker and black coloured (magnetic) powder was collected at the centre of the beaker when placed on a Rotamantle. The collected black powder was made into several pellets and annealed at selected temperatures in the range 200-900 °C for
6 h. The prepared samples was denoted as CF_20, CF_50 and CF_90 for annealing temperature at 200 °C, 500 °C and 900 °C, respectively. The heating and cooling rate during annealing in air was maintained @ 5 °C/ min. Selected samples was used for high temperature measurements of synchrotron X-ray diffraction, dc magnetization and current-voltage characteristics.

B. Sample characterization

The X-ray diffraction pattern was recorded using Angle Dispersive X-ray Diffraction (ADXRD) beamline (BL-12) at Indus-2synchrotron radiation facility, RRCAT, Indore, India. The synchrotron X-ray diffraction (SXRD) patterns were recorded in the 20 range 5-40 ° for two selected samples (CF_20 and CF_90) during warming (300 K to 873 K) and cooling (873 K to 300 K) modes of the temperature variation. The wave length was fixed at 0.7820 Å and 0.7600 Å for the samples CF_20 and CF_90, respectively. The beam line consists of a Si (111) based double crystal monochromator and two experimental stations, namely, a six circle diffractometer (Huber 5020) with a scintillation point detector. The high temperature SXRD measurements were performed in air with temperature stabilization for nearly 5 minutes before measurement, at each temperature. Photon energy for SXRD was accurately calibrated by using SXRD pattern of LaB₆ NIST standard in the same set up. The high temperature dc magnetization [M(T)] in the warming mode (300 K-950 K) and cooling mode (back to 300 K) were measured using physical properties measurement system (PPMS-EC2, Quantum Design, USA). The field dependent magnetization [M(H)] curves were recorded within magnetic field range ± 70 kOe at selected temperatures during warming mode after completing the M(T) measurement cycle. The current-voltage (I-V) characteristics of CF_50 and CF_90 samples were measured using Keithley 6517B high resistance meter. The disc shaped samples (⌀ = 10 mm, t ~ 0.5 mm) were placed between two Pt electrodes of a home-made sample holder to make Pt/sample/Pt device structure. The
current passing through the sample was measured by sweeping dc voltage within ± 50 V during warming (W) and cooling (C) modes of the temperature variation in the range 300 K-623 K.

3. RESULTS

A. Synchrotron X-ray diffraction

Fig. 1 shows SXRD pattern of the CF_20 and CF_90 samples at selected temperatures. The Y-axis has been re-scaled for some of the patterns to compare between warming and cooling modes. SXRD pattern at all measurement temperatures (300 K- 873 K) represent the cubic spinel structure (space group Fd3m) for both the samples [3-4]. The crystalline planes corresponding to cubic spinel structure are indexed at the top of Fig. 1(a-b). The patterns showed distinct changes due to variation of annealing temperature (200 °C and 900 °C) of the as-prepared sample and also with the variation of measurement temperatures. SXRD peaks in the CF_20 sample are relatively broad. Although cubic spinel structure is maintained during warming and cooling modes, a structural distortion (amorphous type background) in the 2θ range 32.5-34.5 ° (see inset of Fig. 1(a)) is introduced in CF_20 sample at temperatures 823 K and 873 K. Interestingly, the usual peak intensity ratio was maintained in the sample for the temperatures up to 773 K both in warming and cooling modes of the measurement. However, a sharp peak same as (531) plane is sitting on the amorphous background. This large background introduces a butterfly type wing in the peak. In this temperature range, preferential orientation of the (511) and (440) planes showed an unusual increase of their intensity in contrast to the highest intensity usually observed for the (311) plane. In the absence of any extra peaks, possibility of impurity phase is ruled out, but a non-equilibrium structure is expected due to low annealing temperature (200 °C) [12, 31]. The CFO_90 sample (Fig. 1(b)) showed sharp SXRD peaks with smooth background for both warming and cooling modes. The cubic spinel structure is maintained at temperatures 300 K and
373 K during warming mode. In addition to cubic spinel structure, an extra peak of exceptionally high intensity is seen at 2θ~20° (inset of Fig. 1(b)) for the measurement temperature at 473 K. It represents growth of an additional phase CoO (cubic structure with space group Pm3m) [3], whose crystalline planes are highly oriented along (200) direction. Intensity of the peak of CoO phase decreased at 573 K and finally disappeared at 673 K and 873 K during warming mode. The (200) peak of CoO phase reappeared during cooling mode at higher temperature range 773-573 K and this peak intensity is weak in comparison to that in the temperature range 473-573 K during warming mode. The additional phase of CoO is absent at temperature range 473 K-300 K during cooling mode. This indicates thermal hysteresis in the formation of CoO phase and the cubic spinel structure is reversible at room temperature after cooling back from high temperature.

Apparently, SXRD peaks of cubic spinel structure seem to be fitted with a single phase. A close scrutiny of the shape and asymmetric nature of the peaks indicates possibilities of a two-component structure. Fig. 2 shows the Rietveld refinement of the SXRD patterns at 300 K and 873 K in warming mode using single phase and two phased models of cubic spinel structure. The peak of CoO phase in CF_90 sample has been excluded during fit of cubic spinel phase. The difference in the fit with single component and two components is shown in the insets of Fig. 2 for (333) peak. The two-phased model is the best option for fitting SXRD patterns of the CF_20 sample, although pattern has been fitted with single phase. The difference between positions of a specific peak (e.g., 333) for two components is significantly reduced for CF_90 sample. Table 1 (supplementary) summarizes the obtained parameters using single phase and two-phase models for the CF_20 and CF_90 samples at 300 K and 873 K. Structural refinement was performed by assigning atomic positions close to normal spinel structure of Co3O4 with Wyckoff positions at tetrahedral (8a) sites (1/8, 1/8, 1/8) fully occupied by Co2+ ions (or minor occupancy of Fe3+)
ions), at octahedral (16d) sites (1/2, 1/2, 1/2) co-occupied by Co$^{3+}$ and Fe$^{3+}$ ions, and at 32e sites occupied by oxygen (O$^{2-}$) ions. Some of the parameters (e.g., isotropic thermal displacements ($B$), occupancy of the Co atoms at tetrahedral sites and Fe at octahedral sites) were suitably refined. The final refinement was carried out by allowing the variation of oxygen parameter ($u$) and using two approaches. In the first approach, occupancy of O atoms at 32e sites was allowed to vary by fixing the occupancy of Co atoms to 1.75 at 16d sites. In the second approach, the occupancy of Co atoms at 16d sites was allowed to vary by fixing the occupancy of O atoms to 4 at 32e sites. In case of single phase model, the structural parameters (lattice parameter ($a$), oxygen parameter ($u$)) and the refinement parameters ($R_p$, $R_{wp}$, $R_{exp}$, $\chi^2$) are not much different for both the approaches. The oxygen content and composition of metal ions in spinel structure are nearly matched to stoichiometric composition of the samples at room temperature (300 K), where as composition of the samples determined from structural refinement at 873 K showed excess O atoms (alternatively deficiency of Co atoms at octahedral sites) per formula unit of the spinel structure. In case of two phased model, we have denoted the Co rich phase as phase 1 (A sites are fully occupied by Co ions and Fe content at octahedral sites is assigned less amount than the assigned value for single phase) and the Fe rich phase as phase 2 (where Co and Fe are allowed to occupy both A and B sites and the total Fe content is more than the assigned value for single phased model).

Fig. 3(a-h) shows temperature variation of the structural parameters (lattice constant ($a$), oxygen parameter ($u$), difference of Co content ($\delta$Co) at B sites with reference to the expected value 1.75 when O content is fixed at 4, and difference of O content ($\delta$O) with reference to expected value 4 when Co content at B sites fixed at 1.75) obtained from the fit of SXRD data using single phase model. The irreversible trajectories suggest micro-structural changes during
thermal cycling process. The lattice parameter \((a)\) and oxygen parameter \((u)\), as shown in Fig. 3, were obtained from the fit where O content was fixed to 4 and Co content at octahedral sites was allowed to vary. The lattice parameter increases with temperature due to thermal expansion of the material. The oxygen parameter \((u)\), an additional parameter that defines the exact position of O atoms with reference to the regular tetrahedron at 8a sites and octahedron at 6d sites, lies between 0.24 and 0.275 for spinel oxides [32, 33]. The \(u\) values are a bit scattered (range 0.259-0.264) for CF_20 sample, where as \(u\) values (0.261-0.264) showed a decreasing trend on increasing temperature for CF_90 sample. The \(u\) values greater than 0.26 shows displacement of O ions away from ideal positions along (111) direction. The decreasing trend of \(u\) with increase of measurement temperature indicates the expansion of B sites at the expense of A sites. We have calculated the M-O (metal-oxygen) bond length for CF_90 sample at A sites \((R_{\text{tet}})\) and B sites \((R_{\text{oct}})\) using the formula \(R_{\text{tet}} = a\sqrt{3}(u-\frac{1}{6})\) and \(R_{\text{oct}} = a\sqrt{(3u^2 - 2u + \frac{3}{2})}\) [32]. The smaller M-O bond lengths correspond to the presence of cations with higher (+3) oxidation state (smaller ionic radius), where as the larger M-O bond lengths correspond to the presence of cations with lower (+2) oxidation state in the lattice sites [1, 33]. Although annealing temperature around 900 \(^0\)C thermodynamically forms the single phase cubic spinel structure in Co rich spinel oxide [12], our results indicate the possibility of exchanging Co and Fe ions between A and B sites or the variation of charge state of the cations during increase of the measurement temperature. The M-O bond length at A sites decreases by \(\sim 1.53\%\) (1.963 to 1.933 Å) on increasing the temperature from 300 K to 873 K by increasing the M-O bond length \(\sim 1.19\%\) (1.936 to 1.959 Å) at B sites. This allows absorption of excess oxygen atoms at the B sites and forms defective spinel structure at higher temperatures. The \(\delta\)Co values are slightly positive at temperatures below 400 K and
showed a decreasing trend with negative values at higher temperatures in both the samples, except a noticeable fluctuation with positive values at the temperatures 573 K and 673 K during warming mode of the CF_20 sample. In the cooling mode, $\delta$Co values are slightly smaller (and negative) than that in warming mode for CF_90 sample, whereas $\delta$Co remained at slightly positive values at temperatures below 773 K for CF_20 sample. The excess O content in the samples increases at higher temperatures and the increase is remarkably higher in CF_20 sample. The results suggest that non-equilibrium structure of CF_20 sample is highly sensitive to thermal cyclic effect and single phase is not a good model to fit its SXRD data. On the other hand, the refinement of SXRD patterns using two-phased model is poor for CF_90 sample. Hence, profile fit (without assignment of site distribution of atoms) of the SXRD patterns was used to determine lattice parameter for CF_90 sample using two phased model. The temperature dependence of lattice parameters of the two-phased structure is shown in the insets of Fig. 3(a, e). It differed noticeably between Co rich phase (phase 1) and Fe rich phase (phase 2) for CF_20 sample. The minor difference for CF_90 sample confirms nearly equilibrium (single phase) lattice structure.

We determined SXRD peak profile parameters (intensity, position ($2\theta$) and full width at half maximum ($\beta$)) were obtained by fitting selected peaks using Lorentzian shape. Intensity of the peaks at different temperatures, normalized by the peak intensity at 300 K in warming mode, are shown in Fig. 4 for CF_20 sample (left side) and CF_90 sample (right side). The intensity for crystalline planes of the spinel structure showed irreversible effect with higher intensity during warming mode and lower peak intensity during cooling mode of the measurements. Intensity of the peaks from (111), (311) and (400) planes at lower scattering angles decreases on increasing the temperature. Especially, intensity of the (111) peak approaches down to zero at 873 K for CF_20 sample. Intensity of this peak is high, although decreases at higher temperatures, for
CF_90 sample. The decrease of (111) peak intensity is sensitive to increasing number of cation defects in spinel structure [25, 34]. Intensity of the crystalline planes (422, 333, 440) at higher scattering angles initially decreases in the temperature range 300 K-473 K, followed by an unusual increase with a broad maximum around 673 K and then, decreases above 800 K for both the samples during warming mode. Intensity of these peaks showed an increasing trend on decreasing the temperature during cooling mode of CF_20 sample, where as the intensity of CF_90 sample showed a decreasing trend. The crystallite size (<D>) and micro-strain (ε) in the samples were calculated using Williamson-Hall equation:

$$\beta \cos \theta = \frac{0.89 \lambda}{D} + 2 \varepsilon \sin \theta,$$

where λ is wavelength of synchrotron X-ray radiation. Fit of the data at 300W (300 K during warming mode) is shown in Fig. 5(a-b). Crystallite size and micro-strain are shown in Fig. 5(c-d) and Fig. 5(e-f), respectively. The total change of crystallite size and micro-strain is considerably small for temperatures in the range 300 K-873 K, but a thermal cycling effect on the variation of these micro-structural parameters is observed during warming and cooling modes of the measurement, and also on increasing the annealing temperature. The crystallite size and micro-strain in CF_20 sample increased with measurement temperature with a local minimum at about 773 K, although irreversible effect is observed between warming and cooling modes within a bit scattered data. As an effect of high temperature annealing, crystallite size (23.0-23.4 nm) increased in CF_90 sample with smaller micro-strain (0.073-0.077) in comparison to smaller crystallite size (1.95-2.25 nm) and larger micro-strain (0.16-0.21) in CF_20 sample.

B. dc magnetization

Fig. 6 shows the magnetization curves during field warming (MFW(T)) and field cooling (MFC(T)) modes of the temperature variation under constant magnetic field at 100 Oe or 500 Oe. The MFW(T) curves gradually decreased at temperatures higher than the magnetic blocking
temperature, which is visible above 300 K (the case of CF_50 sample at 375 K for field 100 Oe) or below 300 K by combining low temperature magnetization data (as the case of CF_20 sample at 270 K for field 100 Oe and as the case of CF_90 sample at 230 K for field 500 Oe and at 300 K for field 100 Oe). An unusual increment in the MFW(T) curves is observed above a typical temperature $T_{0}^{\text{MFW}}$ that depends on annealing temperature of the samples (e.g., 684 K, 690 K and 700 K for the samples CF_20, CF_50 and CF_90, respectively). A local broad maximum is observed at about 880 K for all the samples. Similar unusual properties in MFW(T) at higher temperatures were observed in Fe deficient Fe$_{3-x}$Ti$_{x}$O$_4$ spinel oxide [25]. An extrapolation of the MWF(T) curve for CF_90 sample indicates a possible $T_C$ at about 995 K for the Co doped $\gamma$-Fe$_2$O$_3$ (maghemite) like phase, instead of $\gamma$-Fe$_2$O$_3$ (maghemite) phase with $T_C$ at about 1100 K. On reversing the temperature down to 300 K without changing the applied magnetic field (field cooling mode), the MFC(T) curves followed different paths without any local magnetization maximum. Instead, the MFC(T) curves sharply increased below a typical temperature $T_{C}^{\text{MFC}}$ (~705 K for CF_20 and CF_50 samples, and 820 K for CF_90 sample). A wide gap between MFC(T) and MFW(T) curves suggests anisotropic magnetic properties in thermal cyclic process along with a substantial change in spin order during cooling mode. The temperature derivative of the MFW curves ($d\text{MFW}/dT$) intercepted on temperature axis at the onset point ($T_{0}^{\text{MFW}}$) of the unusual increment of high temperature magnetization, whereas shoulder position in the $d\text{MFC}/dT$ curves matches to the onset point ($T_{C}^{\text{MFC}}$) of sharp magnetization increment during field cooling mode. The height of unusual high temperature maximum dominates over the low temperature maximum at about 300 K or below in the case of CF_90 sample, whereas the low temperature maximum dominates over the high temperature maximum for the samples with low annealing temperature. The high temperature (> 650 K) magnetic features in the present samples
are different from the magnetic behavior below the $T_N$ of NiFe$_2$O$_4$ [35], $\alpha$-Fe$_2$O$_3$ (hematite) [36] and Cr doped $\alpha$-Fe$_2$O$_3$ [37].

The M(H) curves (Fig. 7 (a-c)) were recorded at selected temperatures by increasing the temperature from 300 K in the field range +70/50 kOe down to -5 kOe. The samples showed ferrimagnetic features with hysteresis loop and lack of magnetic saturation at higher fields. The M(H) data were also recorded at 300 K before subjecting to any high temperature measurements. As shown in the insets of Fig. 7 (b-c), the in-field thermal recycling (300 K to 950 K and back to 300 K) modified magnetic properties and exhibited higher magnetic moment at 300 K than the magnetic moment at pre-thermal cycling condition. In order to understand the dilution in ferrimagnetic order and determine the spontaneous magnetization ($M_S$), we have used Arrot plot (H/M vs. $M^2$) [29] and shown $M^2$ vs. H/M plot (Fig. 7(d-f)) for convenience. An extrapolation of the linear or polynomial fit of high filed $M^2$ vs. H/M curves on positive value of $M^2$ axis at H/M = 0 corresponds to $M_S^2(T)$ below the Curie point ($T_C$) of a ferro/ferrimagnet. The $M^2$ vs. H/M showed a linear curve at higher fields and a sharp decrease at lower fields with positive slope for all the samples at 300 K. An upward curvature at higher magnetic fields and a negative slope at lower fields for the temperatures at and above 350 K/375 K were observed in case of the CF_20 and CF_50 samples (low annealing temperatures), and at 650 K and above in the case of CF_90 sample. According to Banerjee criterion [38], the slope of H/M vs. $M^2$ plot is positive (negative) for second-order (first-order) phase transition. In the present samples, negative slope in H/M vs. $M^2$ plot continuously increased on increasing the measurement temperature above 300 K. The temperature dependence of $M_S$ values using Arrot plot are shown in the inset of Fig. 8(a) and the $M_S$ values using a direct linear fit of the high field M(H) curve are shown in Fig. 8(a)). In both the cases, $M_S$ value decreased on increasing measurement temperature and rate of the decrement
became slow above 700 K. There was no unusual peak in $M_S(T)$ curves above 700 K as seen in the MFW(T) curves. The $M_S$ values are found to be higher for the samples with low temperature annealing (CF_20 and CF_50) at temperatures below 600 K. However, temperature dependent remanent magnetization ($M_R$) of the CF_20 sample indicted lower values than the CF_50 and CF_90 samples (Fig. 8(b)). Coercivity ($H_C$) increased with annealing temperature of the samples. An increment of the coercivity ($H_C$) values (Fig. 8(c)) at higher temperatures may be associated with onset of an additional strain induced magnetic phase above 600 K, which of course depends on annealing temperature of the samples.

C. Current-voltage characteristics and Electrical conductivity

The I-V characteristics at selected temperatures by cycling the measurement temperature during warming and subsequent cooling modes. After completing the measurement during first cycle (W1C1), the measurement was repeated during second cycle (W2C2) of the temperature variation. Fig. 9 (a-b) shows I-V characteristics of the CF_50 sample at selected temperatures during W1C1 and W2C2 cycles. I-V characteristics are identical for both the cycles, although differences are noted during warming (low conductivity) and cooling (high conductivity) modes. The CF_90 sample showed similar I-V characteristics. Fig. 9 (c) shows I-V curves during W2C2 cycle for CF_90 sample. In both the samples, I-V characteristics for the positive bias voltage are identical to the characteristics for negative bias voltage. It confirms proper electrical contact on both sides of the disc-shaped sample. The resistance ($R= V/I$) of the samples at bias voltages +5 V, +20 V and +40 V were calculated from the I-V curves. Fig. 9 (d-f) shows the resistance of the samples at different temperatures. The R(T) curves showed high resistance state during warming mode and low resistance state during cooling mode. As shown in Fig. 9(d-e) for CF_50 sample, the irreversible feature and magnitude of the resistance appeared larger during first cycle of
measurement than the second cycle measurement. Interestingly, R(T) curves transformed from an unusual metal like state to usual semiconductor state above the temperature $T_{MSW}$ during warming mode and semiconductor to metal like state below the temperature $T_{SMC}$ during cooling mode. Recently, many spinel oxides have shown such unusual electronic properties above 300 K [39-41]. The observed metal like state may not be a true metallic state as free electrons are not generally expected in spinel oxides. However, trapping and de-trapping of the electronic charge carriers (electrons and holes) in the defect induced localized states at the edges of conduction (CB) and valence (VB) bands can contribute to metal like state (positive temperature coefficient of resistance) in spinel oxide [40]. The temperature $T_{MSW}$ (~ 443 K) in warming mode of the first cycle for CF_50 sample is found to be higher than the value (~ 373 K) in the second cycle and the same value (373 K) is found for CF_90 sample. On the other hand, the temperature $T_{SMC}$ is found at about 330 K for both the samples and irrespective of the repetition of cycles. The R(T) curves in the semiconductor state was fitted with Arrhenius law: $R(T) = R_0 \exp \left( \frac{E_a}{k_B T} \right)$. The fit of the lnR vs 1000/T data at 5 V are shown in the insets of Fig. 9(a-c). The activation energy ($E_a$) of the CF_50 sample is found to be notably high 3.413 eV during warming mode in comparison to 0.635 eV in the cooling mode of W1C1 cycle. The theoretical calculation [1] suggested that high concentration of defects and local cation disorder in Co rich spinel oxide can increase the band gap. In the W2C2 cycle, activation energy decreased to 0.679 eV and 0.617 eV during warming and cooling modes, respectively. Stabilization of the activation energy both in warming and cooling modes of the W2C2 cycle can be attributed to micro-structural changes in the system, where absorbing and releasing capacity of oxygen atoms is decreased during repeated heating cycles [42]. The activation energy of the (high temperature annealed) CF_90 sample in W2C2 cycle was found 0.99 eV and 0.67 eV during warming and cooling modes, respectively.
The activation energy in our samples are comparable to the values in spinel oxides [39, 43]. In addition to thermal activated charge conduction mechanism, we analyzed I-V characteristics at different temperatures using power law ($I = I_0V^n$) to understand space charge effect. The values of $I_0$ (constant current at bias voltage tends to zero) and exponent ($n$) were obtained from the intercept on current axis and slope, respectively using the log-log plot of I-V curves. Examples are shown for the data at 300 K and 573 K (Fig. 10 (a-b)). The linear fit in the log-log plot of I-V curves shows reasonably good description of power law. The data at all the temperatures are fitted with two slopes. The slope ($n_1$) at low voltage regime is found to be smaller in comparison to the slope ($n_2$) at high voltage regime (above 10 V). Fig. 10 (c-k) shows temperature variations of the fit parameters ($n_1$ and $n_2$ with corresponding current values $I_{01}$ and $I_{02}$) during warming and cooling modes of the W2C2 cycle. Temperature dependence of the constant current values from the power law fit in the low and high voltage regimes showed irreversibility effect (low current in warming mode and high current in cooling mode). It seems to be correlated with $R(T)$ curves. The $n_1$ values of CF_50 sample lie in the range 1-1.2 below $T_{MSW} \sim 373$ K and stabilized around 1 for the temperatures above 373 K during warming mode. In cooling mode, the $n_1(T)$ curve showed similar features with relatively higher values of $n_1$ in comparison to the values in warming mode. In case of CF_90 sample, the $n_1$ values lie in the range 1-1.1 and there is not much difference between the $n_1(T)$ curves during warming and cooling modes. The $n_1(T)$ curves of CF_90 sample showed an increasing trend with temperature in contrast to the decreasing trend for CF_50 sample. The $n_1$ values close to 1 shows Ohmic behaviour in the low voltage regime. The $n_2(T)$ curves showed slightly higher values (1-1.8). This suggests interfacial space charge influence in the conduction mechanism at higher voltage regime [44]. The irreversibility effect is also seen in the $n_2(T)$ curves between warming and cooling modes. The $n_2(T)$ curve in CF_50
sample showed an increasing trend at the temperatures below and above 400 K during warming mode. It showed higher values during cooling mode and a local maximum around 450 K. In case of CF_90 sample, the $n2(T)$ curve showed higher values during warming mode in contrast to the values during cooling mode. The $n2(T)$ curve decreased with the increase of temperature during warming mode, where as it showed a local maximum around 500 K during cooling mode. Then, $n2$ values decreased down to a local minimum at about 373 K, below which $n2$ value increases.

4. DISCUSSION

Recently, defect (intrinsic/extrinsic) induced magnetism in non-magnetic or AFM spinel oxides has emerged as an interesting field of research [24]. In the present spinel oxide, origin of the unit cell is located at the center of symmetry ($\frac{1}{4} \frac{1}{4} \frac{1}{4}$). The cations (Fe and Co ions) occupy A and B sites, and anions (O ions) occupy the 32e positions. Nonstoichiometry of the metal/oxygen ratio incorporates cationic vacancies in the spinel structure ($A_{1-x}B_{2-x_2}[x]O_4$) to preserve the closest oxygen packing or the chemical formula unit can be written as $AB_2O_{4+x}$ to incorporate the excess oxygen [25, 42]. We show that lattice deformation at higher temperatures plays an important role in modifying magnetic and electrical properties. We offer a qualitative discussion. The semiconductor properties in $Co_{x}Fe_{3-x}O_4$ ferrite can be either $p$ type (hole hopping through $Co^{2+}–O^{2–}–Co^{3+}$ superexchange paths for $x > 1$) or $n$ type (electron hopping through $Fe^{3+}–O^{2–}–Fe^{2+}$ superexchange paths for $x < 1$) [11, 43]. Such ideal conditions are not obeyed in defective spinel oxides. A defect free III–II mixed spinel oxides is supposed to be electrically insulator, if all the divalent cations (e.g., $Fe^{2+}$, $Co^{2+}$) occupy A sites and all the trivalent cations (e.g., $Fe^{3+}$, $Co^{3+}$) occupy B sites, and it can be electrically conductive under site exchange of the cations [45]. The occupancy of $Fe^{3+}$ ions at A sites produce electron donors ($n$-type conductivity) and occupancy of the $Co^{2+}$ ions at B sites produce hole-acceptors ($p$-type conductivity). Huang et al. [26]
proposed different intrinsic point defects for CoFe₂O₄, e.g., V₃Co(B), V₃Fe(A), V₃O, Co(B)₃Fe(A), Co(B)₃Fe(B), Fe(B)₃Co(B), [Co(B)₃Fe(A), Fe(A)₃Co(B)]. The V₃Co(B) represents the vacancy of Co ions at the B sites; V₃Fe(A) represents the vacancy of Fe ions at A sites; Co(B)₃Fe(A) represents the vacancy of Fe ions at A sites substituted by Co ions at B sites, and [Co(B)₃Fe(A), Fe(A)₃Co(B)] represents exchange between Co ion at the B site and Fe ion at the A site. In case of an oxygen ion vacancy (V₃O), two electrons are produced per defect site (O₃O → [V₃O₀⁺2e⁻] + $\frac{1}{2}$O₂(g)) and removal of these electrons gives oxygen vacancy with +2 charges (V₃O₂⁺). Similarly two holes are produced per defect site of a Co²⁺ ion (cation) vacancy (Co₃Co → [V₃Co₀⁺2h⁺] + Co(s)) and removal of these holes gives Co²⁺ ion vacancy with -2 charges (V₃Co²⁻). Hence, cation vacancies at B sites under oxygen rich condition increases p type electronic conductivity in cubic spinel structure. On the other hand, energy for creating V₃Fe(B) and V₃Co(B) defects are high in the metal (Co/Fe) rich condition, tending toward 4.72 eV and 3.69 eV, respectively. The formation energy of V₃Fe(B) in the metal-rich region is higher than that in the Co-rich (Fe poor) region. The formation energy of V₃Fe(A) is high under all environments, tending toward 7.20 eV, 5.68 eV and 3.69 eV under metal rich, Co rich and oxygen rich conditions, respectively. Similarly, formation energy of V₃O can go up to 3.72 eV in oxygen rich condition in comparison to 0.86 eV under metal rich condition. On the other hand, small formation energy (~0.65 eV) for [Co(B)₃Fe(A), Fe(A)₃Co(B)] allows exchange between Fe(A) and Co(B) ions in spinel oxide. The exceptionally high activation energy (3.4 eV) during warming mode of the W1C1 cycle of CF_20 sample could be attributed to formation of V₃Fe(A) and V₃O defects under oxygen rich condition in spinel oxide. This is in contrast to the small formation energy (~0.62-0.99 eV) for V₃O defects under metal rich condition or [Co(B)₃Fe(A), Fe(A)₃Co(B)] defects during cooling mode of W1C1 and also during W2C2 cycles of the I-V curves measurements.
At higher temperatures under oxygen rich environment, intrinsic vacancy of Co\(^{2+}\) ions is expected in the lattice structure following the mechanism Co\(^{2+}\) + \(\frac{z}{2}\)O \(\rightarrow\) zCo\(^{3+}\) + (1-z) Co\(^{2+}\) + \(\frac{z}{2}\)O\(^2-\); 
z is the fraction of Co\(^{2+}\) ions that has been converted to Co\(^{3+}\) ions. In normal cubic spinel oxide like Co\(_3\)O\(_4\) with distribution of cations (Co\(^{2+}\))\(_A\)\[Co^{3+}\]Co\(^{3+}\]\(_B\)O\(_4\), the A site atoms are in +2 charge state and occupy 1/8 of the tetrahedral holes, while the B site atoms are generally +3 charge state and occupy 1/2 of the octahedral holes. Rest of the lattice spaces lie vacant and expansion of lattice space at higher temperature allows adsorption of additional oxygen atoms. In the present spinel oxide, a small fraction of B site Co\(^{3+}\) ions are replaced by Fe\(^{3+}\) ions and a fraction (z) of the Co\(^{2+}\) ions at A sites can be converted into Co\(^{3+}\) ions. The V\(_{Co(A)}\) is not energetically favourable, but it can be exchanged with Fe ion at B sites by forming Fe\(_A\)Co\(_B\) defect [26]. According to the model proposed by Readman and O'reilly [25], the adsorption and ionization of oxygen atom result in the creation of new sites at A and B sublattices. The created A sites will be filled with Co\(^{2+}\) ions, and each new B site will be filled by Fe\(^{3+}\)/Co\(^{3+}\) ions. A fraction of the cations in B sites, highly mobile at high temperature, diffuses into the surface of the grains by creating vacancies at B sites. Thus, a skin of \(\gamma\)-Fe\(_2\)O\(_3\) (maghemite) or Co doped \(\gamma\)-Fe\(_2\)O\(_3\) like phase is formed under oxygen rich condition at higher temperatures. The interior and skin of the grains rapidly become homogenous within B sites due to migration of vacancies and exchange of Fe\(^{3+}\) and Co\(^{3+}\) ions. At the same time, the population of cations at A sites becomes homogeneous by the movement of electrons between interior Co\(^{2+}\) ions and surface Fe\(^{3+}\) ions. This gives rise to additional electron hopping conductivity between cations at A sites in the material at higher temperatures. This shows overall enhancement of electrical conductivity at higher temperatures and also at the samples of low annealing temperature due to high concentration of defects. The magnetic enhancement at 300 K after in-field thermal cyclic process arises due to magnetic
change in the core (interior)-shell structure. Such heterogeneous spin structure introduces first order magnetic phase transition [28, 29]. In Bean-Rodbell theory [30], the molecular mean field theory was modified by taking into account a linear coupling between magnetization and cell volume to explain first-order magnetic transition in disordered magnetic materials. According to Bean-Rodbell theory, distorted lattice structure introduces a strain induced energy that increases free energy. A compromise happens in the system to lower its free energy by distorting the lattice in a direction that increases magnetic exchange energy (Curie temperature). A linear relationship between the exchange constant ($\lambda$) and Curie temperature with the change of cell volume ($V$) and strength of magneto-elastic coupling ($\beta$) has been expressed by Nielson et al [29] as $\lambda = \lambda_0(1+\beta \frac{V-V_0}{V_0})$ and $T_C = T_0(1+\beta \frac{V-V_0}{V_0})$. Here, $\lambda_0$, $T_0$ and $V_0$ are the exchange constant, the unit cell volume and Curie temperature in the material without magneto-elastic coupling, respectively. In first order phase transition materials [29-30], the free energy may have two minima in M(T, H) curves corresponding to meta-stable and stable states. The meta-stable state is reflected in the MFW(T) curves, whereas MFC(T) curves represent a stable state. The FM-PM transition temperature ($T^{MFW}_C$) in MFW(T) curves is expected to be higher than the PM-FM transition temperature ($T^{MFC}_C$) in MFC(T) curves. In the inter-mediate phase between these two transitions, a thermal hysteresis (MFC(T) < MZFC(T)) is observed upon cooling the system because the material still remains in PM state until a temperature close to the "true" Curie point ($T^{MFC}_C$) is reached to re-establish its FM state. Based on the experimental data, we define $T^{MFW}_0$ (~ 680 K-700 K) as the Curie temperature of clamped structure (less lattice distortion) and $T^{MFW}_C$ (~ 995 K) as the Curie temperature of free structure (strong lattice distortion). In the MFC(T) curves, the estimated $T^{MFC}_C$ values are found to be close to $T^{MFW}_0$ for CF_20 and CF_50 samples, where as a substantial difference ($T^{MFC}_C > T^{MFW}_0$) is noted for CF_90 sample.
This is attributed to two-phased lattice structure with higher lattice strain and magnetic moment and smaller electrical resistance at temperatures below 650 K for the CF_20 sample in contrast to a nearly single phased cubic spinel lattice structure (except appearance of CoO phase for a short temperature range) in association with smaller lattice strain and magnetic moment and higher electrical resistance for the CF_90 sample. The characteristic differences in CF_90 sample are realized from its $T_C^{MFC}$ noticeably higher than $T_0^{MFW}$ and coercivity in defect induced magnetic state is smaller than the samples at low temperature annealing. The chemical composition of the present spinel oxide (with a small replacement of Co by Fe) is close to the typical normal spinel oxide $\text{Co}_3\text{O}_4$, which is an AFM with $T_N$ in the range 30-40 K [46-47]. Hence, smaller magnetic moment ($M_S$) in CF_90 sample below 650 K represents its lattice and magnetic structure close to equilibrium state in comparison to highly non-equilibrium lattice and magnetic structure of the samples with low temperature annealing [31].

The DFT calculations for CoFe$_2$O$_4$ [26] showed that DOS contours for defective structure are similar to that of defect-free spinel oxides, except extra levels are seen near the VB or CB within the band gap due to defects. In the case of $V_{\text{Co(B)}}^0$, there are some occupied levels with spin up (↑) states at the Fermi energy and some unoccupied levels with spin up states in the band gap. Hence, $V_{\text{Co(B)}}^0$ introduce acceptor like level in the band gap and also similar contribution for $V_{\text{Fe}}^0$ both at A and B sites. In contrast, $V_{\text{O}}^0$ induces the extra donor like level occupied by two electrons in the upper part of band gap. The local ordering of the 3d electronic spins of Co and Fe ions in doubly and triply degenerated $e_g$ and $t_{2g}$ levels of octahedral sites control the magnetic spin order and charge hopping process at B sites of the spinel structure [1]. Each Co$^{2+}$ ion at A sites contains three unpaired electrons at $t_{2g}$ level and at B sites contains one unpaired electron at $t_{2g}$ level and two unpaired electrons at $e_g$ level, respectively. Each A site or B site Fe$^{3+}$ ion
contains five unpaired electrons at \( e_g \) and \( t_{2g} \) level. On the other hand, each \( \text{Co}^{3+} \) ion at B sites results nearly zero moment. So, magnetic moment in defect free spinel structure is determined by the site exchange of \( \text{Fe}^{3+} \) (~3.91 \( \mu_B \)) and \( \text{Co}^{2+} \) (~2.52 \( \mu_B \)) ions. Considering order of unpaired 3d electronic spins of \( \text{Co}^{2+} \) and \( \text{Fe}^{3+} \) ions at B sites in opposite directions with respect to A sites, the cation defects affects the net magnetic moment \( (M = M_B - M_A) \) in spinel structure, especially the \( V_{\text{Fe}(B)} \) and \( \text{Co}(B)_{\text{Fe}(B)} \) defects reduce net moment and presence of \( V_{\text{Fe}(A)} \) increases net moment. The oxidation of surface cations in oxygen rich environment controls the magnetic and electronic properties. It is highly sensitive to surface response along (111) direction [34]. The crystalline structure of \( \text{Co}_3\text{O}_4 \) spinel oxide along (111) direction has been modeled as a sequence of \( \text{Co}^{3+}/\text{Co}^{2+} \) ion layers separated by layers of O ions. The surface can by either be B-terminated (formed by \( \text{Co}^{3+} \) ions) or A-terminated (formed by \( \text{Co}^{2+} \) and \( \text{Co}^{3+} \) ions) or oxidized on the A (AO) or B (BO) surfaces. The disruption of coordination of the surface ions can produce dangling bonds and subsequently, new energy levels (defined as surface induced states) in the energy gap. In case of the AO and BO terminated surfaces the band gap contains extra states located near the Fermi level. The extra states are partially filled by \( d \)-orbitals of Co ions and \( p \)-orbitals of O ions. The number of extra states increases for systems with A- or B-terminated surface. The strongly delocalization of electron states, which almost fill the forbidden gap, gives rise to metal like character. The \( \text{Co}^{2+} \) ions at A and AO-terminated surfaces have magnetic moment close to that in bulk. The \( \text{Co}^{3+} \) ions are nonmagnetic in bulk, but they have a magnetic moment close to that of \( \text{Co}^{2+} \) ions at the B-terminated surface and substantially smaller (non-zero) at the BO surface. The O ions at the AO- and BO-surfaces show nonzero magnetic moment due to polarization of their \( p \)-orbitals. The A and AO surfaces contribute AFM properties owing to A-A superexchange interactions, unlike FM properties in B and BO surfaces due to B-B superexchange interactions.
5. CONCLUSIONS

We studied the lattice structure and magnetic properties of the $\text{Co}_{2.75}\text{Fe}_{0.25}\text{O}_{4+\delta}$ ($\delta$: 0-0.68) spinel oxide. The structure becomes non-stoichiometric during high temperature measurement of magnetic and electrical properties and re-gains stoichiometric value on reversing back to room temperature. The non-equilibrium lattice structure at higher measurement temperatures showed preferential orientations along (511) and (440) directions for the sample at low temperature (200 °C) annealing, where as an additional phase of CoO with preferential (200) plane orientation and thermal hysteresis behavior appeared for the sample at annealed at 900 °C. The lattice distortion in the cubic spinel structure at higher measurement temperatures is more prominent for the samples at low temperature annealing in comparison to the sample annealed at 900 °C. The samples exhibited irreversible effect in the structure, magnetic and electrical properties between warming and cooling modes of the measurements. The material exhibited meta-stable magnetic state with two magnetic transitions during field warming mode, where as the defect induced magnetic transition at higher temperature is suppressed during field cooling mode and a stable magnetic state with low Curie temperature was observed. The magnetic disorder introduced a first order phase transition. The high temperature electrical conductivity, including unusual metallic like state, has been understood by the formation of defect induced magnetic spin order at the surfaces of the grains and surface states at the band gap.

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Table 1 (supplementary). Rietveld refinement parameters

(a) SXRD data at 300W fitted with single cubic spinel structure for CF_20 sample

| Atoms (sites) | occupancy of O fixed to 4.0 and Co(16d) variable | occupancy of Co(16d) fixed to 1.750 and O variable |
|---------------|-------------------------------------------------|--------------------------------------------------|
|               | Wyckoff positions | B | Occupancy | Wyckoff positions | B | Occupancy |
| Co(8a)  | 0.12500 | 0.12500 | 0.12500 | 0.97 | 1.000 | 0.12500 | 0.12500 | 0.12500 | 0.97 | 1.000 |
| Fe(8a)  | 0.12500 | 0.12500 | 0.12500 | 0.97 | 0.000 | 0.12500 | 0.12500 | 0.12500 | 0.97 | 0.000 |
| Fe(16d) | 0.50000 | 0.50000 | 0.50000 | 0.97 | 0.250 | 0.50000 | 0.50000 | 0.50000 | 0.97 | 0.250 |
| Co(16d) | 0.50000 | 0.50000 | 0.50000 | 0.97 | 1.789(3) | 0.50000 | 0.50000 | 0.50000 | 0.97 | 1.750 |
| O (32e) | 0.25971(16) | 0.25971(16) | 0.25971(16) | 0.78 | 4.000(0) | 0.26020(33) | 0.26020(33) | 0.26020(33) | 0.78 | 3.962(29) |

Cell parameter (a) = 8.10094 (28) Å, volume (V) = 531.626 (32) Å³

\( R_p: 3.50, R_{wp}: 4.51, R_{exp}: 2.29, \chi^2: 3.88 \)

(b) SXRD data at 873W fitted with single cubic spinel structure for CF_20 sample

| Atoms (sites) | occupancy of O fixed to 4.0 and Co(16d) variable | occupancy of Co(16d) fixed to 1.750 and O variable |
|---------------|-------------------------------------------------|--------------------------------------------------|
|               | Wyckoff positions | B | Occupancy | Wyckoff positions | B | Occupancy |
| Co(8a)  | 0.12500 | 0.12500 | 0.12500 | 0.97 | 1.000 | 0.12500 | 0.12500 | 0.12500 | 0.97 | 1.000 |
| Fe(8a)  | 0.12500 | 0.12500 | 0.12500 | 0.97 | 0.000 | 0.12500 | 0.12500 | 0.12500 | 0.97 | 0.000 |
| Fe(16d) | 0.50000 | 0.50000 | 0.50000 | 0.97 | 0.250 | 0.50000 | 0.50000 | 0.50000 | 0.97 | 0.250 |
| Co(16d) | 0.50000 | 0.50000 | 0.50000 | 0.97 | 1.727(8) | 0.50000 | 0.50000 | 0.50000 | 0.97 | 1.750 |
| O (32e) | 0.26009(30) | 0.26009(30) | 0.26009(30) | 0.78 | 4.000(0) | 0.26210(24) | 0.26210(24) | 0.26210(24) | 0.78 | 4.653(28) |

Cell parameter (a) = 8.12867 (53) Å, volume (V) = 537.103 (61) Å³

\( R_p: 4.35, R_{wp}: 5.63, R_{exp}: 3.17, \chi^2: 3.15 \)
(c) SXRD data at 300W fitted with single cubic spinel structure for CF_90 sample

| Atoms (sites) | occupancy of O fixed to 4.0 and Co(16d) variable | occupancy of Co(16d) fixed to 1.750 and O variable |
|--------------|--------------------------------------------------|---------------------------------------------------|
|              | Wyckoff positions | B Occupancy | Wyckoff positions | B Occupancy |
| Co(8a)       | X 0.12500 Y 0.12500 Z 0.12500 | 0.97 1.000 | X 0.12500 Y 0.12500 Z 0.12500 | 0.97 1.000 |
| Fe(8a)       | X 0.12500 Y 0.12500 Z 0.12500 | 0.97 0.000 | X 0.12500 Y 0.12500 Z 0.12500 | 0.97 0.000 |
| Fe(16d)      | X 0.50000 Y 0.50000 Z 0.50000 | 0.97 0.250 | X 0.50000 Y 0.50000 Z 0.50000 | 0.97 0.250 |
| Co(16d)      | X 0.50000 Y 0.50000 Z 0.50000 | 0.97 1.774(8) | X 0.50000 Y 0.50000 Z 0.50000 | 0.97 1.750 |
| O (32e)      | X 0.26327(32) Y 0.26327(32) Z 0.26327(32) | 0.78 4.000(0) | X 0.26365(28) Y 0.26365(28) Z 0.26365(28) | 0.78 4.049(29) |

Cell parameter (a) = 8.16672 Å, volume (V) = 544.682(14) Å³

R_p: 9.43, R_wp: 12.4, R_exp: 10.94, \( \chi^2 \): 1.28

(d) SXRD data at 873W fitted with single cubic spinel structure for CF_90 sample

| Atoms (sites) | occupancy of O fixed to 4.0 and Co(16d) variable | occupancy of Co(16d) fixed to 1.750 and O variable |
|--------------|--------------------------------------------------|---------------------------------------------------|
|              | Wyckoff positions | B Occupancy | Wyckoff positions | B Occupancy |
| Co(8a)       | X 0.12500 Y 0.12500 Z 0.12500 | 0.97 1.000 | X 0.12500 Y 0.12500 Z 0.12500 | 0.97 1.000 |
| Fe(8a)       | X 0.12500 Y 0.12500 Z 0.12500 | 0.97 0.000 | X 0.12500 Y 0.12500 Z 0.12500 | 0.97 0.000 |
| Fe(16d)      | X 0.50000 Y 0.50000 Z 0.50000 | 0.97 0.250 | X 0.50000 Y 0.50000 Z 0.50000 | 0.97 0.250 |
| Co(16d)      | X 0.50000 Y 0.50000 Z 0.50000 | 0.97 1.738(11) | X 0.50000 Y 0.50000 Z 0.50000 | 0.97 1.750 |
| O (32e)      | X 0.26127(50) Y 0.26127(50) Z 0.26127(50) | 0.78 4.000(0) | X 0.25910(73) Y 0.25910(73) Z 0.25910(73) | 0.78 4.069(64) |

Cell parameter (a) = 8.18966 Å, volume (V) = 549.285(22) Å³

R_p: 10.5, R_wp: 13.8, R_exp: 12.57, \( \chi^2 \): 1.20

R_p: 10.3, R_wp: 13.7, R_exp: 12.56, \( \chi^2 \): 1.19
(e) SXRD data at 300W fitted with two-phased model of cubic spinel structure for CF_20 sample

| Atoms (sites) | Co rich phase (O variable) | Fe rich phase (site occupancy of cations adjusted, O variable) |
|----------------|-----------------------------|---------------------------------------------------------------|
|                | Wyckoff positions | B | Occupancy | Wyckoff positions | B | Occupancy |
| X | Y | Z | | X | Y | Z | |
| Co(8a) | 0.12500 | 0.12500 | 0.12500 | 0.97 | 1.000 | 0.12500 | 0.12500 | 0.12500 | 0.97 | 0.850 |
| Fe(8a) | 0.12500 | 0.12500 | 0.12500 | 0.97 | 0.000 | 0.12500 | 0.12500 | 0.12500 | 0.97 | 0.150 |
| Fe(16d) | 0.50000 | 0.50000 | 0.50000 | 0.79 | 0.050 | 0.50000 | 0.50000 | 0.50000 | 0.79 | 0.190 |
| Co(16d) | 0.50000 | 0.50000 | 0.50000 | 0.79 | 1.950 | 0.50000 | 0.50000 | 0.50000 | 0.79 | 1.750 |
| O (32e) | 0.26119(28) | 0.26119(28) | 0.26119(28) | 0.72 | 3.947(23) | 0.26250(48) | 0.26250(48) | 0.26250(48) | 0.72 | 4.640(54) |

Cell parameter (a) = 8.10992 (30) Å, volume (V) = 533.396(34) Å³

Co rich phase (Bragg R-factor: 4.57, phase fraction: 65.69%)
Fe rich phase (Bragg R-factor: 4.95, phase fraction: 34.31%)

| Atoms (sites) | Co rich phase (Co at 16d sites variable) | Fe rich phase (site occupancy of cations adjusted, Co at 16d sites variable) |
|----------------|-----------------------------|---------------------------------------------------------------|
|                | Wyckoff positions | B | Occupancy | Wyckoff positions | B | Occupancy |
| X | Y | Z | | X | Y | Z | |
| Co(8a) | 0.12500 | 0.12500 | 0.12500 | 0.97 | 1.000 | 0.12500 | 0.12500 | 0.12500 | 0.97 | 0.850 |
| Fe(8a) | 0.12500 | 0.12500 | 0.12500 | 0.97 | 0.000 | 0.12500 | 0.12500 | 0.12500 | 0.97 | 0.150 |
| Fe(16d) | 0.50000 | 0.50000 | 0.50000 | 0.79 | 0.050 | 0.50000 | 0.50000 | 0.50000 | 0.79 | 0.190 |
| Co(16d) | 0.50000 | 0.50000 | 0.50000 | 0.79 | 2.026(7) | 0.50000 | 0.50000 | 0.50000 | 0.79 | 1.602(17) |
| O (32e) | 0.26047(27) | 0.26047(27) | 0.26047(27) | 0.72 | 4.000 | 0.26212(59) | 0.26212(59) | 0.26212(59) | 0.72 | 4.000 |

Cell parameter (a) = 8.11062 (30) Å, volume (V) = 533.535 (34) Å³

Co rich phase (Bragg R-factor: 4.77, phase fraction: 64.81%)
Fe rich phase (Bragg R-factor: 6.21, phase fraction: 35.19%)
Fig. 1 Synchrotron XRD pattern measured in the temperature range 300-873 K during warming and cooling modes for the CF_20 (a) and CF_90 (b) samples. Inset shows additional disorder/phase at higher temperatures.
Fig. 2 Rietveld refinement patterns of the CF_20 (a) and CF_90 (b) samples fitted with single phase and two phases for the experimental data at 300W and 873W. The insets clarify the single phased and two-phased fit for (333) peak.
Fig. 3 Structural parameters obtained from Rietveld refinement (single phase) of high temperature SXRD patterns of the CF_20 (a-d) and CF_90 (e-h) samples. The inset of (a,e) show lattice parameters for two-phased model of the samples.
Fig. 4. Temperature dependence of SXRD peak intensity in warming and cooling modes.
Fig. 5 Fit of the SXRD peak parameters at 300 K during warming mode using Williamson-Hall equation (a-b). Temperature dependence of crystallite size (c-d) and micro-strain (e-f) of the samples in warming and cooling modes.
Fig. 6 Temperature dependence of the magnetization of the samples under magnetic field warming (MFW) and field cooling (MFC) modes (a-c) and derivative of the corresponding MFW and MFC curves of the samples (d-f). The observed magnetic transition temperatures are marked by vertical lines. The inset shows low temperature magnetic data (M_LT) alongwith high temperature magnetic data (M_HT).
Fig. 7 M(H) curves at different temperatures for the Co$_{2.75}$Fe$_{0.25}$O$_4$ ferrite samples (a-c). The insets of (b-c) compare the M(H) curve of the sample measured at 300 K before (pre) and after (post) high temperature magnetization measurements in field warming and cooling modes. The $M^2$ vs. $H/M$ plot of high temperature $M(H)$ data (d-f).
Fig. 8 The spontaneous magnetization ($M_s$) was calculated from linear extrapolation of high field $M(H)$ data (a) and also from $M^2$ vs. $H/M$ plot (inset). The coercivity ($H_c$) and remanent magnetization ($M_R$) were calculated from $M(H)$ loop of the samples.
Fig. 9 The I-V characteristics at selected temperatures during warming and cooling modes of CF_20 (a-b) and CF_90 (c) samples. The insets show the lnR vs. 1000/T plot at bias voltage +5V. The temperature dependence of resistance of the samples calculated at 5 V, 20 V and 40 V during warming and cooling modes of the measurement (d-f).
Fig. 10 Current vs. voltage curves at 300 K and 573 K in log-log scale to show power law fit (a-b). Temperature variation of the current (c-f) and corresponding exponent (g-j) values at low and high voltage regimes for the samples CF_50 and CF_90, respectively.