

Structural heterogeneity and magnetic interaction evolution in $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ nanoferrites with a minor α -Fe secondary phase

Truong-Tho Nguyen^a, Tran Thi Ngoc Nha^{b,c}, Dang Ngoc Toan^{d,e}, Dinh Thanh Khan^f,
Le Thi Tuyet Ngan^g, Tran Dang Thanh^h, Do Hung Manh^h, Pham Thanh Phong^{b,c,*}

^a Faculty of Electronics, Electrical Engineering and Material Technology, University of Sciences, Hue University, Hue, 530000, Viet Nam

^b Laboratory of Magnetism and Magnetic Materials, Science and Technology Advanced Institute, Van Lang University, Ho Chi Minh City, Viet Nam

^c Faculty of Applied Technology, Van Lang School of Technology, Van Lang University, Ho Chi Minh City, Viet Nam

^d Institute of Research and Development, Duy Tan University, Danang, 550000, Viet Nam

^e Faculty of Natural Sciences, Duy Tan University, Danang, 550000, Viet Nam

^f The University of Danang-University of Science and Education, Danang, 550000, Viet Nam

^g Faculty of Engineering and Technology, University of Information & Communication Technology, Thai Nguyen University, Thai Nguyen City, Viet Nam

^h Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi, Viet Nam

ARTICLE INFO

Keywords:

Ferrites
 $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$
Wasp-waisted hysteresis
Dipolar interaction
Interacting superparamagnetic
Modified Langevin scaling

ABSTRACT

The magnetic behavior of spinel ferrite nanoparticles is strongly influenced by nanoscale structural heterogeneity and phase evolution induced during synthesis. In this work, $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.3, 0.5$, and 0.7) nanoparticles were synthesized by thermal decomposition to investigate the influence of Mn substitution on structural evolution and magnetization reversal. X-ray diffraction coupled with Rietveld refinement revealed the coexistence of spinel ferrite and a minor metallic α -Fe phase in the $x = 0.3$ and $x = 0.5$ samples, whereas the $x = 0.7$ sample exhibited a single-phase spinel structure within the instrumental detection limit. Increasing Mn content progressively suppressed the α -Fe phase, reduced the ferrite crystallite size from ~ 24 to ~ 9 nm, and increased lattice microstrain, indicating enhanced local structural heterogeneity. These structural changes were accompanied by a systematic evolution of the magnetic behavior. The α -Fe-containing samples exhibited constricted hysteresis loops arising from magnetic heterogeneity, whereas the single-phase ferrite $x = 0.7$ sample showed thermally activated magnetic relaxation together with increasing dipolar interaction effects, as supported by FC/ZFC magnetization, Kneller analysis, dipolar field estimation, and modified Langevin scaling. The results demonstrate that Mn substitution effectively controls phase evolution and magnetic reversal mechanisms in Co-Mn ferrite nanoparticles, providing a coherent framework for understanding the transition from heterogeneous blocked ferrimagnetic behavior to an interacting-superparamagnetic-like regime.

1. Introduction

Magnetic spinel ferrites have attracted considerable attention because of their tunable magnetic properties, high electrical resistivity, chemical stability, and broad technological applications in electronic, optical, and biomedical fields [1–3]. Their general formula, MFe_2O_4 ($\text{M} = \text{divalent metal ion}$), provides substantial compositional flexibility through cation substitution and redistribution between tetrahedral (A) and octahedral (B) sites, enabling the modulation of magnetic exchange interactions and functional properties [4–8]. Among various spinel ferrites, cobalt ferrite (CoFe_2O_4) is particularly attractive owing to its high coercivity (H_c), large magnetocrystalline anisotropy (K_1),

and moderate saturation magnetization (M_s), making it a promising material for magneto-optical devices, magnetic separation, magnetic resonance imaging, targeted drug delivery, and magnetic hyperthermia applications [9–12]. The structural and magnetic properties of CoFe_2O_4 -based nanostructures, however, are governed not only by their chemical composition but also by cation distribution, crystallinity, particle morphology, and local structural disorder introduced during synthesis [1,15,16].

Cation substitution has therefore been widely employed to tailor the structural and magnetic properties of spinel ferrites. In particular, Mn substitution in CoFe_2O_4 has attracted considerable interest because Mn^{2+} ions can modify the cation occupancy at A and B sites, thereby altering

* Corresponding author. Science and Technology Advanced Institute, Van Lang University, Viet Nam.

E-mail addresses: ntthokh@hueuni.edu.vn (T.-T. Nguyen), phamthanhhong@vlu.edu.vn (P.T. Phong).

the competing A-B and B-B superexchange interactions. Nevertheless, previous studies have reported markedly different magnetic behaviors for Co-Mn ferrites prepared by different synthesis routes. For example, Yadav et al. [17] observed enhanced saturation magnetization and remanent magnetization after Mn substitution in cobalt ferrite synthesized by the auto-combustion method. In contrast, Reddy et al. [18] reported reduced M_s but increased H_c with increasing Co concentration in hydrothermally synthesized $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles (NPs). Similarly, Ali A. Ati et al. [19] observed non-monotonic variations in both M_s and H_c for co-precipitated $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ NPs, whereas P. Monisha et al. [20] reported simultaneous decreases in M_s and H_c with increasing Mn content. These contrasting observations indicate that the magnetic evolution of Co-Mn ferrites cannot be fully explained by the nominal Mn/Co composition alone.

One factor that has received comparatively little attention is the possible deviation from ideal Fe stoichiometry during synthesis. Most structure-property correlations implicitly assume chemically homogeneous and stoichiometric ferrite phases. However, thermal decomposition and other wet-chemical synthesis methods may introduce Fe-related compositional deviations or Fe-rich secondary phases, resulting in local structural and magnetic heterogeneity. Such deviations may influence charge compensation, cation redistribution, phase stability, and magnetic exchange interactions, thereby modifying the overall magnetic response. Despite its potential importance, the influence of Fe non-stoichiometry and the associated structural heterogeneity on the magnetic behavior of Mn-substituted cobalt ferrites has not yet been systematically investigated.

Structural heterogeneity is particularly important because it may alter magnetization reversal through the coexistence of magnetically distinct regions or through magnetic coupling between different phases. Constricted (wasp-waisted) hysteresis loops are generally associated with magnetic systems containing components with different switching fields or coupling strengths, such as core-shell nanoparticles and hard-soft magnetic composites [21–23]. Similar hysteresis features have also been reported for ferrite nanoparticles and have been attributed to intrinsic magnetic inhomogeneity within nominally single-phase materials [7,24,25]. However, the origin of these anomalous magnetic characteristics in Mn-substituted cobalt ferrites remains uncertain because they may arise from intrinsic structural disorder, compositional heterogeneity, Fe non-stoichiometry, or the formation of Fe-rich secondary phases. In particular, although constricted hysteresis loops have been reported in ferrite-based systems containing Fe-related secondary phases, the specific contribution of the α -Fe phase to the magnetization reversal process has not been systematically clarified.

In this work, $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.3, 0.5$, and 0.7) NPs were synthesized by the thermal decomposition method to investigate how Fe non-stoichiometry and the associated structural heterogeneity influence the magnetic behavior. X-ray diffraction combined with Rietveld refinement, Raman spectroscopy, EDX analysis, TEM characterization, and comprehensive magnetic measurements were employed to correlate phase evolution, cation redistribution, and magnetic interactions. Particular emphasis was placed on understanding the origin of constricted hysteresis loops and the evolution of the relative contributions of exchange and dipolar interactions. By integrating structural characterization with magnetic analyses, including the Law of Approach to Saturation and dipolar field estimation, this work contributes to a better understanding of how Fe non-stoichiometry and nanoscale structural heterogeneity influence magnetization reversal in Mn-substituted cobalt ferrite nanoparticles.

2. Experimental section

2.1. Synthesis of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.3, 0.5$ and 0.7) NPs

$\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.3, 0.5$ and 0.7) NPs were synthesized via a thermal decomposition route following a previously reported procedure

[26] with slight modifications. Cobalt(II) acetylacetonate (99%, Acros, USA), manganese acetylacetonate hydrate (Sigma-Aldrich 97%), and iron(III) acetylacetonate (99%, Acros, USA) were used as metal precursors. Oleic acid (97%, Fisher Scientific, USA) and oleylamine (80–90%, Acros, USA) served as surfactants, while benzyl ether (99%, Thermo Scientific, USA) was used as the solvent. In addition, 1-octadecanol (95%, Acros, USA) was employed as a reducing agent. Ethanol and n-hexane (95%, Daejung, Korea) were used for washing and purification without further treatment.

The stoichiometric amounts of Co, Mn, and Fe precursors corresponding to $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ compositions were added into a 100 mL three-neck flask containing a mixed solution of oleic acid (18 mmol), oleylamine (18 mmol), 1-octadecanol, and 40 mL of benzyl ether. The reaction mixture was initially heated to 110 °C and maintained for 1 h to remove residual moisture and low-boiling impurities. Subsequently, the temperature was increased to 250 °C and held for 30 min, followed by further heating to 275 °C for 1 h under a nitrogen atmosphere with continuous reflux condensation.

After naturally cooling to room temperature, the obtained nanoparticles were magnetically separated and repeatedly washed with ethanol and n-hexane to remove residual organic species and excess surfactants. The purified products were subsequently dried in a vacuum oven at 200 °C for 4 h to obtain $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs. Subsequent XRD/Rietveld refinement detected no additional iron oxide phases within the instrumental resolution.

2.2. Characterization of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.3, 0.5$ and 0.7) NPs

The crystal structure of the $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.3, 0.5$ and 0.7) NPs was examined using a Bruker D8 ADVANCE Eco X-ray diffractometer equipped with Cu-K α radiation ($\lambda = 0.154$ nm). X-ray diffraction (XRD) patterns were collected over the 2θ range of 10°–80° with a step size of 0.004°. Structural parameters and phase analysis were further evaluated by Rietveld refinement using the GSAS-II software package.

The elemental composition and spatial distribution of the constituent elements in the $x = 0.3$ and $x = 0.7$ samples were characterized by energy-dispersive X-ray spectroscopy (EDX) attached to a field-emission scanning electron microscope (FESEM, Hitachi S-4800, Japan). The morphology and particle size of the $x = 0.7$ sample were examined by high-resolution transmission electron microscopy (HR-TEM, JEM-2100, JEOL, Japan).

Magnetic measurements were carried out using a vibrating sample magnetometer (VSM, PPMS VersaLab). Magnetization as a function of the applied magnetic field was measured in the field range from –30 to +30 kOe at different temperatures. The magnetic anisotropy and temperature-dependent coercivity behavior were further analyzed using the Law of Approach to Saturation (LAS) and Kneller's model, respectively.

Raman spectra were obtained using an XploRA PLUS micro-Raman spectrometer (Horiba) with a 785 nm excitation laser to investigate the vibrational characteristics of the $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs. The spectra were recorded over the range of 50–1000 cm^{-1} , with the low-frequency limit enabled by the instrument configuration, allowing reliable detection of low-wavenumber lattice vibrational modes. A microscope objective with a magnification of 100 $\times$ was used, and the laser power was adjusted to avoid local heating effects during measurement.

3. Results and discussion

3.1. Structural and compositional characterization

The X-ray diffraction (XRD) patterns and corresponding Rietveld refinement profiles of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.3, 0.5$, and 0.7) NPs are presented in Fig. 1. The Rietveld refinement was performed using the crystallographic models of cubic spinel ferrite (space group $Fd\bar{3}m$, COD No. 1533163) and body-centered cubic α -Fe (space group $Im\bar{3}m$, COD No.

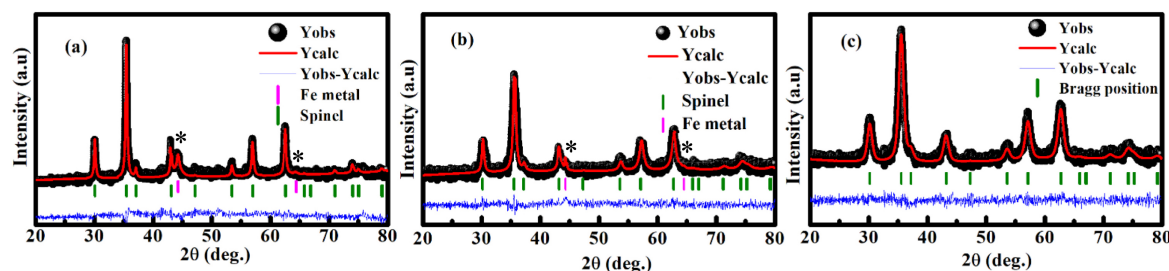


Fig. 1. X-ray diffraction patterns and Rietveld refinement profiles of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs: (a) $x = 0.3$, (b) $x = 0.5$, and (c) $x = 0.7$. The experimental data, calculated profiles, Bragg reflection positions, and difference curves are shown for each refinement. The additional reflections marked by (*) in panels (a) and (b) are assigned to the metallic α -Fe phase with a body-centered cubic structure (space group $Im\bar{3}m$).

9013476). The diffraction profiles of the $x = 0.3$ and $x = 0.5$ samples are satisfactorily fitted using a two-phase structural model consisting of a spinel ferrite phase and a metallic α -Fe phase, whereas the $x = 0.7$ sample is satisfactorily refined using only the spinel ferrite phase, indicating a single-phase ferrite structure within the instrumental detection limit. The characteristic diffraction peaks of the spinel ferrite phase are observed in all samples, confirming that the ferrite matrix retains the cubic spinel structure throughout the investigated composition range. In addition, weak reflections at approximately $2\theta \approx 44.7^\circ$ and 65° are observed only for the $x = 0.3$ and $x = 0.5$ samples and are indexed to the (110) and (200) planes of metallic α -Fe, respectively. Their inclusion in the Rietveld refinement yields α -Fe weight fractions of approximately 7.3 wt% and 2.5 wt% for $x = 0.3$ and $x = 0.5$, respectively, whereas no detectable α -Fe phase is identified for $x = 0.7$. To further highlight the characteristic α -Fe reflection, an enlarged XRD profile in the 2θ range of 40 – 50° comparing all three compositions is provided in the Supplementary Information (Fig. S1), clearly illustrating the progressive suppression of the α -Fe (110) reflection with increasing Mn content.

The refined structural parameters, including the lattice parameter (a), unit-cell volume (V), phase fractions, and refinement reliability factors (R_{wp} , R_p , R_{bkg} , and GOF), are summarized in Table 1. The good agreement between the observed and calculated diffraction profiles, together with the low refinement residuals, supports the reliability of the adopted structural models. It is noteworthy that no additional diffraction peaks corresponding to iron oxide phases, such as Fe_3O_4 , γ - Fe_2O_3 , or α - Fe_2O_3 , are detected within the instrumental resolution. Therefore, the Fe-related secondary phase identified in the $x = 0.3$ and $x = 0.5$ samples is assigned to metallic α -Fe rather than oxidized iron oxide phases.

The formation of the metallic α -Fe phase is likely associated with the phase evolution occurring during thermal decomposition. The incorporation of Fe species into the spinel lattice is governed by local diffusion kinetics, charge compensation, and the availability of divalent Co^{2+} and Mn^{2+} cations during nucleation and crystal growth. Under the present synthesis conditions, kinetically limited cation redistribution may locally hinder complete incorporation of Fe into the spinel framework, resulting in the coexistence of a minor α -Fe phase with the spinel ferrite matrix. As the Mn concentration increases under the present synthesis conditions, the amount of α -Fe decreases markedly, suggesting that Mn incorporation modifies the crystallization pathway and promotes stabilization of the spinel ferrite phase. This behavior may be related to the relatively weaker crystal-field-driven site preference of Mn^{2+} . Nevertheless, the

present results do not establish an intrinsic critical Mn concentration for complete suppression of α -Fe formation; rather, they indicate that, under the present synthesis conditions, the structural evolution changes from a ferrite/ α -Fe two-phase system ($x = 0.3$ and 0.5) to a single-phase spinel ferrite ($x = 0.7$).

The gradual increase in R_{wp} with increasing Mn content indicates a reduced agreement between the experimental and calculated diffraction profiles. Such variation may arise from several factors, including peak broadening, increased microstrain, local lattice distortion, cation redistribution, or subtle deviations from the ideal structural model. Therefore, R_{wp} is not considered as a direct measure of structural disorder. Instead, the structural disorder and lattice distortion are evaluated based on the microstrain analysis, diffraction peak broadening, and composition-dependent structural evolution discussed below. From a magnetic perspective, the coexistence of spinel ferrite and metallic α -Fe in the $x = 0.3$ and $x = 0.5$ samples introduces two magnetic phases with markedly different magnetic anisotropy and saturation magnetization. Such structural heterogeneity is expected to contribute to the observed constricted hysteresis behavior and provides a structural framework for the subsequent discussion of magnetization reversal and the Law of Approach to Saturation (LAS).

A systematic decrease in lattice constant and unit cell volume is observed with increasing Mn content, from $8.3912 \text{ \AA}$ and $590.857 \text{ \AA}^3$ for $x = 0.3$ to $8.3438 \text{ \AA}$ and $580.896 \text{ \AA}^3$ for $x = 0.7$, respectively. Although Mn^{2+} generally possesses a larger ionic radius than Co^{2+} , the observed lattice reduction indicates that the structural evolution cannot be interpreted solely on the basis of ionic size. Instead, the observed lattice reduction is likely governed by the combined effects of cation redistribution, local lattice strain and cation redistribution between tetrahedral and octahedral sites.

For the α -Fe phase, the refined lattice parameter decreases slightly from $2.891 \text{ \AA}$ ($x = 0.3$) to $2.889 \text{ \AA}$ ($x = 0.5$), although both values remain larger than that of bulk bcc Fe ($2.866 \text{ \AA}$) [27]. This deviation suggests that the segregated α -Fe regions may retain residual lattice strain and/or incorporate small amounts of transition-metal species during thermal decomposition. The higher α -Fe fraction observed in the Co-rich compositions further suggests that phase separation is more favorable at lower Mn contents under the present synthesis conditions.

Table 1

Structural parameters and Rietveld refinement reliability factors of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.3, 0.5$, and 0.7) NPs, including lattice constant (a), unit cell volume (V), phase fraction (PF) and refinement indicators (R_{wp} , R_p , R_{bkg} and GOF) for the spinel ferrite and α -Fe phases.

x	Ferrites phase			α -Fe metal phase		Refinement indicators			
	a ($\text{\AA}$)	V ($\text{\AA}^3$)	PF (%)	a ($\text{\AA}$)	PF (%)	R_{wp}	R_p	R_{bkg}	GOF
0.3	8.3912	590.857	92.66	2.890	7.34	7.18	5.70	7.99	0.225
0.5	8.3573	583.720	97.51	2.887	2.49	10.09	8.05	10.70	0.230
0.7	8.3438	580.896	100	-	-	12.92	10.27	12.10	0.228

3.2. Crystallite size, strain evolution, and microstructural analysis

Within the framework of the Uniform Deformation Model (UDM), X-ray diffraction peak broadening in nanocrystalline systems arises from the combined contributions of finite crystallite size, lattice microstrain, and instrumental broadening. The instrumental broadening contribution was determined using a LaB₆ standard (NIST SRM 660c) measured under identical instrumental conditions and was subtracted from the experimental peak widths prior to analysis. In the present work, the Lorentzian form of the Williamson-Hall (WH) approach was employed to phenomenologically separate the size- and strain-related broadening contributions according to Eqs. (1) and (2) [28,29].

$$\beta_{\text{total}} = \beta_{\text{size}} + \beta_{\text{strain}} + \beta_{\text{inst}} \quad (1a)$$

$$\beta_{\text{correct}} = \beta_L = \beta_{\text{total}} - \beta_{\text{inst}} = \beta_{\text{size}} + \beta_{\text{strain}} \quad (1b)$$

$$\beta_L \cos \theta = \frac{K\lambda}{D_L} + 4\langle \varepsilon_L \rangle \times \sin \theta \quad (2)$$

where β_{total} represents the experimentally measured full width at half maximum (FWHM), β_{inst} is the instrumental broadening contribution obtained from the LaB₆ standard, and β_{correct} corresponds to the corrected Lorentzian broadening component. The parameters D_L and $\langle \varepsilon_L \rangle$ represent the Lorentzian crystallite size and average lattice strain, respectively. A shape factor of $K = 0.94$, commonly adopted for approximately spherical nanocrystalline domains, was used. The WH analysis was performed using the corrected FWHM values of six diffraction reflections of the spinel ferrite phase, namely (220), (311), (400), (422), (511), and (440). The fitting uncertainties of the extracted crystallite size and lattice strain values are included in Table 2.

The Lorentzian WH analysis reveals a systematic decrease in the average crystallite size of the spinel ferrite phase from approximately 24 nm to 9 nm with increasing Mn concentration, accompanied by an increase in the average lattice microstrain from 0.17×10^{-3} to 1.15×10^{-3} . The simultaneous reduction in crystallite size and enhancement of microstrain suggest that Mn substitution influences the crystallization behavior of the spinel ferrite phase, leading to smaller coherent diffraction domains and enhanced local lattice distortion. This behavior may be associated with composition-dependent with composition-dependent cation redistribution and the different crystal-field characteristics of Mn²⁺ compared with Co²⁺, which can influence local structural relaxation and configurational complexity within the spinel framework.

Table 2

Williamson-Hall-derived crystallite size and lattice microstrain of the spinel ferrite phase and Scherrer-estimated crystallite size of the α -Fe phase.

Sample	Ferrites phase		α -Fe metal phase
	D_L (nm)	$\varepsilon_L (\times 10^{-3})$	D (nm)
x = 0.3	24.3(4)	0.17(3)	11.4(3)
x = 0.5	21.2(3)	0.24(2)	13.1(9)
x = 0.7	9.2(8)	1.14(7)	-

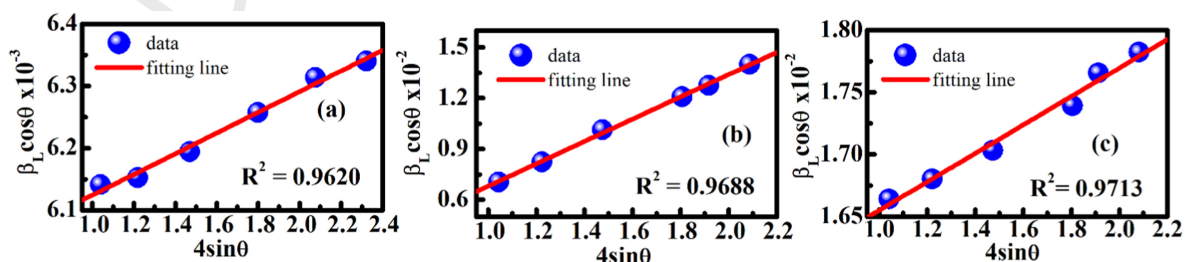


Fig. 2. Williamson-Hall plots using the Uniform Deformation Model (UDM) for Co_{1-x}Mn_xFe₂O₄ (x = 0.3, 0.5, and 0.7) NPs. The crystallite size (D_L) and lattice microstrain ($\langle \varepsilon_L \rangle$) of the spinel ferrite phase were obtained from the linear fitting.

The Lorentzian Williamson-Hall plots for all investigated compositions are presented in Fig. 2. Following correction for instrumental broadening, the approximately linear relationships observed in the WH plots support the applicability of the UDM approach for evaluating the respective contributions of crystallite size and lattice microstrain in the spinel ferrite phase. The corresponding structural parameters, crystallite sizes, and microstrain values are summarized in Table 2.

For the metallic α -Fe phase, crystallite size estimation was performed using the Scherrer equation based on the (110) reflection at $2\theta \approx 44.7^\circ$, as this peak exhibited sufficient intensity for reliable line-broadening analysis, whereas the higher-angle reflection was too weak for meaningful deconvolution. The calculated α -Fe crystallite size increases slightly from approximately 11.4 nm to 13.2 nm as Mn content increases from x = 0.3 to x = 0.5. When considered together with the decreasing α -Fe phase fraction obtained from the Rietveld refinement, this trend suggests that Mn substitution influences the evolution of the secondary α -Fe phase during thermal decomposition. Specifically, increasing Mn concentration suppresses the formation of α -Fe while being accompanied by a slight increase in the crystallite size of the remaining α -Fe phase. These observations suggest that Mn substitution affects the structural evolution of both the spinel ferrite matrix and the coexisting α -Fe phase under the present synthesis conditions.

The coexistence of nanoscale spinel ferrite crystallites and α -Fe nanocrystallites indicates a structurally heterogeneous system in which the two phases are expected to exhibit distinct magnetic characteristics because these phases are known to possess markedly different intrinsic magnetic properties. Such structural heterogeneity provides a structural framework for the subsequent discussion of magnetic interactions, magnetization reversal behavior, and the origin of the constricted hysteresis loops.

To investigate the particle morphology and physical size, the x = 0.7 sample was selected for TEM analysis. In addition, EDX elemental mapping was performed on the x = 0.3 and x = 0.7 samples to examine the spatial distribution of the constituent elements. For the x = 0.7 sample, the mapping was used to verify the absence of obvious elemental segregation, whereas for the x = 0.3 sample it served to distinguish the spinel ferrite matrix from the α -Fe secondary phase and to examine their spatial distribution. The corresponding results are presented in Figs. S2 and S3 of the Supporting Information.

Fig. 3(a) shows that the x = 0.7 sample consists predominantly of quasi-spherical nanoparticles. The particle sizes range from 7.5 to 14.5 nm, as summarized in the histogram shown in Fig. 3(b). The particle-size distribution is well described by a Gaussian function, yielding a characteristic particle size (D_{TEM}) of approximately 10.3 nm, corresponding to the peak position of the fitted curve. Unlike the bimodal particle-size distribution reported for Co_{0.2}Mn_{0.8}Fe₂O₄ NPs synthesized by the flash auto-combustion method (8.2 ± 1.5 and 29.1 ± 8.7 nm) [30], the present nanoparticles exhibit a single Gaussian-like size distribution centered at approximately 10.3 nm, indicating a more homogeneous particle population. The absence of a secondary particle-size population in the present sample further suggests a more uniform particle growth under the adopted thermal decomposition conditions. Furthermore, the close agreement between the average crystallite size determined from

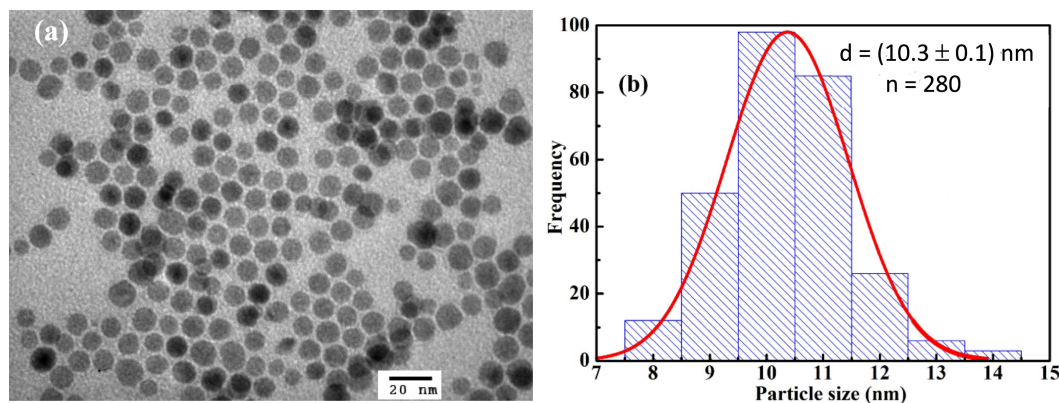


Fig. 3. TEM image (a) and corresponding particle-size distribution histogram (b) of the $x = 0.7$ sample. The average particle size was obtained from statistical analysis of more than 100 nanoparticles.

XRD and the characteristic particle size obtained from TEM suggests that the nanoparticles are predominantly single-crystalline rather than polycrystalline.

The EDX elemental maps (Figs. S2 and S3) provide further insight into the spatial distribution of constituent elements in the $x = 0.3$ and 0.7 samples. For the $x = 0.7$ sample, Co, Mn, Fe, and O exhibit a relatively uniform distribution without detectable elemental segregation within the spatial resolution and detection limits of the measurement, consistent with the formation of a predominantly single-phase spinel ferrite structure. In comparison, the $x = 0.3$ sample shows localized Fe-enriched regions, suggesting a compositional inhomogeneity associated with Fe-rich species. These Fe-enriched regions are consistent with the presence of the α -Fe secondary phase identified by XRD/Rietveld refinement, although EDX mapping alone cannot unambiguously distinguish metallic α -Fe from Fe-containing spinel ferrite. Together with the structural analysis, these results support the composition-dependent evolution from a ferrite/ α -Fe two-phase system at low Mn substitution to a predominantly spinel ferrite phase at higher Mn content.

Taken together, the XRD/Rietveld, TEM, and EDX results consistently indicate that the structural evolution of the investigated $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs is accompanied by composition-dependent nanoscale heterogeneity. Under the present synthesis conditions, increasing Mn content suppresses the formation of the α -Fe secondary phase and promotes stabilization of the spinel ferrite structure. Such structural evolution is expected to influence the relative contributions of exchange and dipolar interactions and therefore provides a structural framework for the discussion of magnetization reversal behavior presented in the following sections.

3.3. Raman spectroscopy analysis

The Raman spectra of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs, together with the corresponding Lorentzian peak deconvolution, are shown in Fig. 4. All samples exhibit the characteristic Raman-active modes of the cubic spinel structure (space group $\text{Fd}\bar{3}\text{m}$, O_h^h symmetry), including the A_{1g} , E_g and T_{2g} modes [5], confirming that the spinel ferrite framework is preserved throughout the investigated compositions. The persistence of these principal vibrational modes is consistent with the preservation of the long-range cubic spinel structure.

However, noticeable composition-dependent variations are observed in the intermediate-frequency region, indicating modifications in the local vibrational environment that are not fully reflected by the average crystallographic structure obtained from XRD. In the Co-rich sample ($x = 0.3$), a Raman band centered at approximately 516.10 cm^{-1} is clearly resolved, whereas its intensity gradually decreases with increasing Mn content. This evolution suggests composition-dependent changes in the local metal-oxygen bonding environment within the spinel lattice. Although these spectral changes may be related to vari-

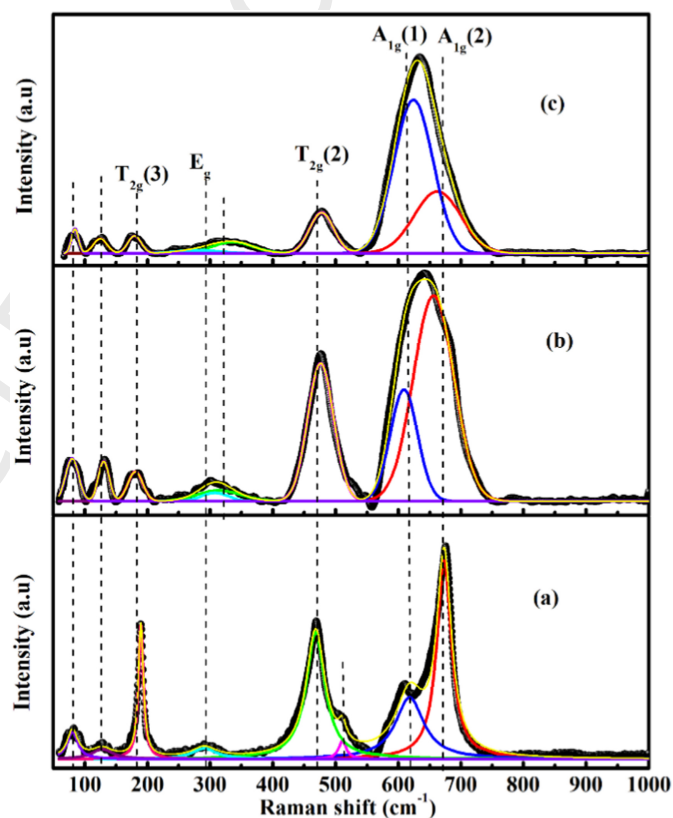


Fig. 4. Raman spectra and Lorentzian deconvolution of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs with $x = 0.3$ (a), 0.5 (b), and 0.7 (c).

ations in the local cation environment, Raman spectroscopy alone does not provide unambiguous information regarding cation occupancy or site distribution.

Concurrently, a broad Raman feature centered at approximately 324.53 cm^{-1} becomes progressively more pronounced for the $x = 0.5$ and $x = 0.7$ samples. The progressive enhancement of this broad feature is consistent with increasing local lattice distortion and reduced short-range structural symmetry accompanying Mn substitution. Together with the XRD/Rietveld refinement and the increase in lattice microstrain obtained from the WH analysis, these observations suggest a gradual increase in local lattice distortion with increasing Mn concentration. Nevertheless, the specific redistribution of cations between tetrahedral and octahedral sites cannot be established solely from the present Raman measurements and therefore is discussed only as a possible structural interpretation.

The low-wavenumber bands observed at approximately 83.76 and 128.77 cm^{-1} were reproducibly detected for all investigated compositions. Since the Raman spectra were recorded over the spectral range of 50–1000 cm^{-1} , these bands are well above the instrumental low-frequency cutoff. They are tentatively assigned to low-frequency lattice vibrations that may become more evident in nanocrystalline ferrites owing to finite crystallite size, lattice strain, and local structural imperfections [31]. However, their specific microscopic origin cannot be uniquely established from the present measurements and therefore no definitive assignment is made.

Although X-ray diffraction and Rietveld refinement confirm the presence of a minor metallic α -Fe phase in the $x = 0.3$ and $x = 0.5$ samples, no corresponding Raman signatures are observed. This behavior is expected because body-centered cubic α -Fe (space group $\text{Im}\bar{3}\text{m}$) is Raman inactive in first-order scattering owing to its crystallographic symmetry and the absence of significant changes in polarizability during lattice vibrations [32]. Moreover, the metallic nature of α -Fe further suppresses Raman scattering because of its high optical reflectivity and limited penetration depth of the excitation laser. Likewise, no Raman bands attributable to iron oxide impurity phases (e.g., Fe_2O_3 or Fe_3O_4) are observed, in agreement with the XRD/Rietveld refinement, which identifies metallic α -Fe as the only detectable secondary phase under the present synthesis conditions.

Overall, the Raman analysis provides complementary evidence that the average structural evolution revealed by XRD is accompanied by composition-dependent modifications in the local vibrational environment. Although Raman spectroscopy does not directly resolve cation occupancy, the observed spectral evolution is consistent with increasing local lattice distortion and short-range structural disorder with increasing Mn content. These local structural variations provide an important link between the average crystallographic structure and the magnetic behavior discussed in the following sections.

3.4. Magnetic properties and interparticle interaction analysis

Fig. 5 presents the temperature-dependent hysteresis loops (55–300 K) of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs, and the corresponding magnetic parameters are summarized in Table 3. Pronounced constricted (waspswaisted) hysteresis loops are observed for the $x = 0.3$ and $x = 0.5$ samples throughout the investigated temperature range. Such constricted hysteresis behavior is generally associated with magnetization reversal in systems containing magnetically distinct components with different switching fields or interaction strengths. In the present samples, this behavior is consistent with the composition-dependent structural heterogeneity revealed by the XRD/Rietveld refinement, WH analysis, Raman spectroscopy, and EDX characterization. For the $x = 0.3$ and $x = 0.5$ samples, this heterogeneity includes the coexistence of the spinel ferrite matrix with a minor α -Fe phase, together with increased lattice microstrain and local structural disorder.

In contrast, the $x = 0.7$ sample exhibits a conventional hysteresis loop without noticeable constriction, suggesting a more homogeneous ferrimagnetic response. This behavior is consistent with the absence of detectable α -Fe within the XRD detection limit and the reduced structural heterogeneity observed for this composition. Although other nanoscale sources of magnetic inhomogeneity cannot be completely excluded, the structural and magnetic results collectively indicate that increasing Mn content suppresses the structural conditions associated with the emergence of constricted hysteresis loops under the present synthesis conditions.

To gain further insight into the magnetic contributions, a semi-quantitative two-phase approximation was employed to estimate the effective saturation magnetization of the $x = 0.3$ and $x = 0.5$ samples. In this approach, the total magnetization is expressed as a weighted contribution from the spinel ferrite matrix and the metallic Fe phase, using the phase fractions obtained from the Rietveld refinement as a first-order approximation:

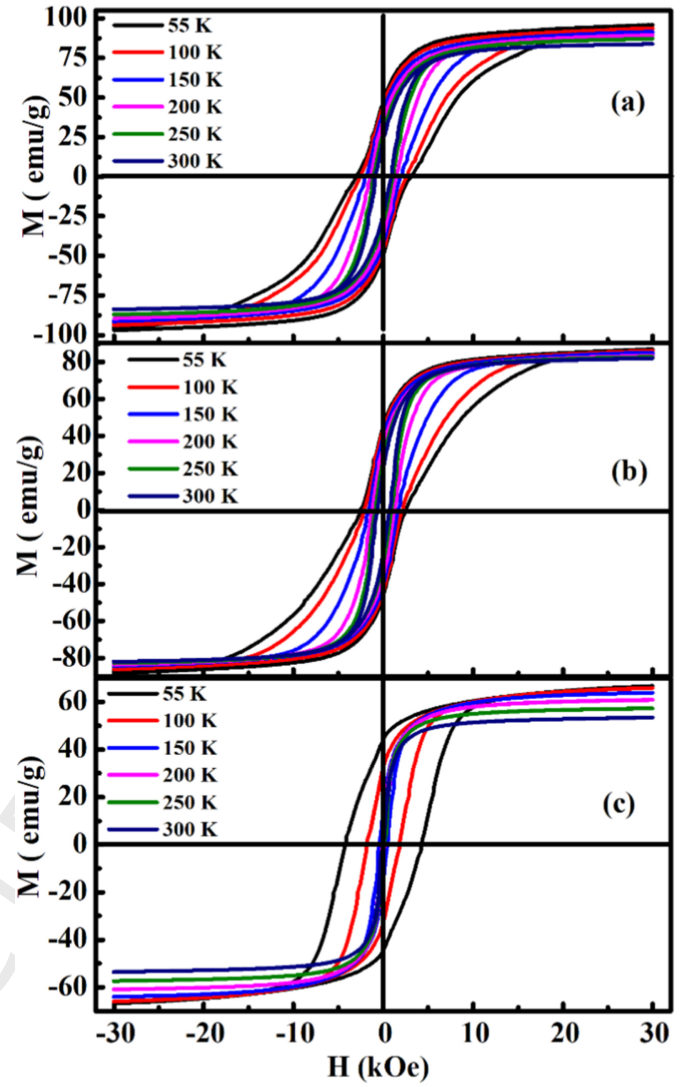


Fig. 5. Temperature-dependent magnetic hysteresis loops of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs measured in the temperature range from 55 K to 300 K: (a) $x = 0.3$, (b) $x = 0.5$, and (c) $x = 0.7$.

$$M_s^{\text{total}} = f_{\text{Fe}} M_s^{\text{Fe}} + (1 - f_{\text{Fe}}) M_s^{\text{Ferrite}} \quad (3)$$

Here, f_{Fe} represents the mass fraction of the metallic α -Fe phase. Considering the nanoscale nature of Fe-rich regions embedded within a chemically stable ferrite matrix, bulk reference values for $M_s^{\text{Fe}}(T)$ were used as a first-order approximation. The temperature dependence of M_s^{Fe} was derived from normalized experimental datasets reported by Cullity and Graham [33], using reduced magnetization scaling with T/T_c . This approach provides a semi-quantitative description of the magnetic contribution of the Fe phase and allows a qualitative comparison between the expected contribution of the metallic phase and the dominant ferrite response.

The high-field magnetization behavior was further analyzed using the Law of Approach to Saturation (LAS) [10]:

$$M(H) = M_s^{\text{total}} \left(1 - \frac{b}{H^2} \right) + \chi_d H \quad (4)$$

where χ_d represents the high-field susceptibility and the b/H^2 term reflects magnetocrystalline anisotropy contributions in the high-field regime. The effective anisotropy constant K_1^{eff} was estimated using:

Table 3

Magnetic parameters of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs measured at different temperatures, including coercivity (H_c), total saturation magnetization (M_s^{total}), remanent magnetization (M_r), squareness ratio (M_r/M_s^{total}) and law-of-approach-to-saturation fitting coefficient (b). The estimated intrinsic saturation magnetization (M_s^{ferrite}) and anisotropy constant (K_1^{ferrite}) of the ferrite phase, together with the corresponding contributions of the metallic α -Fe phase, obtained using the rule-of-mixtures approximation based on Rietveld phase fractions, are also summarized.

a) $x = 0.3$										
Temp. (K)	H_c (Oe)	M_r (emu/g)	M_s^{total} (emu/g)	M_r/M_s^{total}	$b \times 10^6$ (Oe ²)	K_1^{eff} (erg/g)	Ferrite phase		α -Fe phase	
							M_s (emu/g)	$K_1 \times 10^6$ (erg/cm ³)	M_s (emu/g)	$K_1 \times 10^4$ (erg/cm ³)
55	3071.60	47.91	89.15	0.54	3.84	6.33	78.67	3.57	16.25	2.86
100	2650.65	45.51	88.17	0.52	3.55	6.02	77.66	3.40	16.22	2.71
150	1944.74	41.01	86.89	0.47	3.50	5.89	76.32	3.32	16.17	2.56
200	1385.82	35.62	84.87	0.42	2.92	5.25	74.17	2.97	16.14	2.40
250	1109.85	28.75	83.01	0.35	2.53	4.78	72.27	2.70	16.04	2.20
300	903.88	23.04	81.02	0.28	2.23	4.38	70.26	2.47	15.91	2.10
b) $x = 0.5$										
Temp. (K)	H_c (Oe)	M_r (emu/g)	M_s^{total} (emu/g)	M_r/M_s^{total}	$b \times 10^6$ (Oe ²)	K_1^{eff} (erg/g)	Ferrite phase		α -Fe phase	
							M_s (emu/g)	$K_1 \times 10^6$ (erg/cm ³)	M_s (emu/g)	$K_1 \times 10^3$ (erg/cm ³)
55	2559.13	46.03	81.06	0.57	3.25	5.29	77.47	2.89	5.51	9.69
100	2169.43	44.19	80.35	0.55	3.20	5.20	76.75	2.84	5.50	9.18
150	1616.07	40.31	78.90	0.51	2.83	4.81	75.28	2.62	5.49	8.67
200	1212.58	34.90	78.58	0.44	2.76	4.73	74.97	2.58	5.47	8.16
250	883.78	29.73	76.98	0.39	2.36	4.29	73.36	2.34	5.44	7.48
300	673.27	22.48	76.03	0.29	2.17	4.05	72.43	2.21	5.40	7.14
c) $x = 0.7$										
Temp. (K)	H_c (Oe)	M_r (emu/g)	M_s^{total} (emu/g)	M_r/M_s^{total}	$b \times 10^6$ (Oe ²)	$K_1 \times 10^6$ (erg/cm ³)				
55	4224.16	46.03	61.29	0.75	3.90	2.31				
100	1811.58	44.19	60.84	0.73	3.85	2.28				
150	484.72	40.31	59.90	0.67	2.96	1.97				
200	109.92	34.90	58.23	0.60	2.80	1.86				
250	16.51	29.73	55.77	0.53	2.27	1.61				
300	13.42	22.48	53.83	0.41	1.95	1.44				

$$b = \frac{8(K_1^{\text{eff}})^2}{105(M_s^{\text{total}})^2} \quad (5)$$

The resulting effective anisotropy values, summarized in Table 2, reflect the overall magnetic response of the heterogeneous system rather than intrinsic anisotropy constants of individual phases. To provide a first-order estimate of the influence of the metallic phase, a simplified rule-of-mixtures approximation was also considered:

$$K_1^{\text{eff}} = \nu_{\text{Fe}} K_1^{\text{Fe}} + (1 - \nu_{\text{Fe}}) K_1^{\text{ferrite}} \quad (6)$$

where ν_{Fe} denotes the volume fraction of the metallic phase. The temperature-dependent K_1^{Fe} values were obtained from the experimental data compiled by Honda et al. [34]. Given that the magnetocrystalline anisotropy of cobalt ferrites (10^6 – 10^7 erg/cm³) is substantially larger than that of metallic Fe ($\sim 10^5$ erg/cm³), the contribution of the α -Fe phase is expected to represent a secondary perturbation to the overall anisotropy. Accordingly, Eq. (6) is used only as a first-order approxima-

tion to illustrate the possible influence of the metallic phase on the effective anisotropy and is not intended to provide a rigorous micromagnetic description of the heterogeneous system.

Fig. 6 presents the Law of Approach to Saturation (LAS) fitting results obtained in the high-field region ($H \geq 6$ kOe) for all samples at different temperatures. Because the investigated samples contain varying degrees of structural heterogeneity, the extracted values should be regarded as effective anisotropy parameters describing the overall magnetic response rather than intrinsic anisotropy constants of an ideal single-phase ferrite.

To estimate the intrinsic contribution of the spinel ferrite matrix, the first-order rule-of-mixtures approximation described by Eq. (6) was subsequently applied using the α -Fe phase fractions obtained from the Rietveld refinement and the literature values of K_1^{Fe} [34]. The resulting K_1^{ferrite} values therefore represent estimated magnetocrystalline anisotropy constants of the ferrite matrix after accounting for the contribution of the minor α -Fe phase. The temperature-dependent values of K_1^{ferrite} and K_1^{Fe} are summarized in Table 3. The estimated K_1^{ferrite}

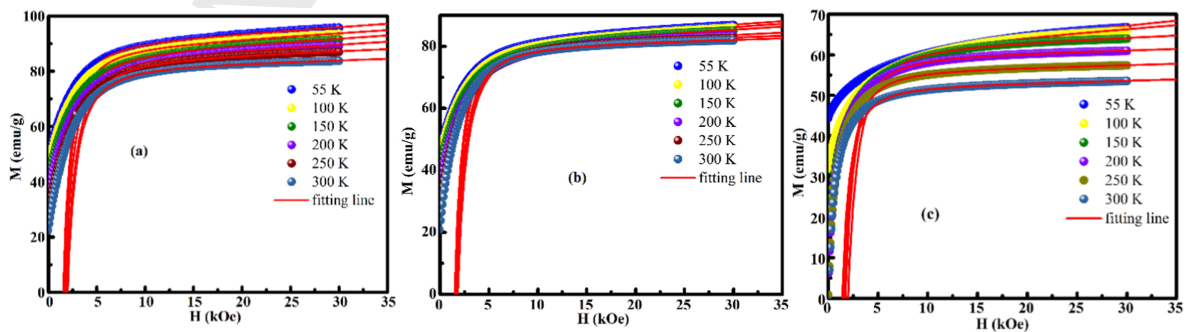


Fig. 6. Experimental and fitted high-field magnetization curves of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs at different temperatures for (a) $x = 0.3$, (b) $x = 0.5$, and (c) $x = 0.7$, analyzed using the law of approach to saturation in the magnetic field region $H \geq 6$ kOe. The solid lines represent the best fits according to Eq. (4), used to estimate the saturation magnetization (M_s^{total}) and effective magnetocrystalline anisotropy constant (K_1^{eff}) for the investigated compositions.

values remain on the order of 10^6 erg cm^{-3} , which is characteristic of cobalt-based spinel ferrites [35]. This result indicates that the effective anisotropy of the investigated samples is dominated by the ferrite matrix, while the contribution of the metallic $\alpha\text{-Fe}$ phase acts primarily as a secondary correction because of its much lower intrinsic magnetocrystalline anisotropy.

Comparison between K_1^{eff} and K_1^{ferrite} shows that the correction for the $\alpha\text{-Fe}$ contribution produces only a modest change in the anisotropy values. This behavior is expected because the intrinsic magnetocrystalline anisotropy of metallic $\alpha\text{-Fe}$ ($\sim 10^4 \text{ erg cm}^{-3}$) is approximately two orders of magnitude smaller than that of cobalt ferrites ($10^6\text{--}10^7 \text{ erg cm}^{-3}$). Consequently, the metallic phase contributes only a minor correction to the overall anisotropy, whereas the dominant contribution remains that of the spinel ferrite matrix.

Furthermore, all samples exhibit systematic temperature-dependent magnetic behavior, with both the total saturation magnetization (M_s^{total}) and coercivity (H_c) increasing as the temperature decreases. Using Eq. (3), the total saturation magnetization was separated into the ferrite (M_s^{ferrite}) and $\alpha\text{-Fe}$ (M_s^{Fe}) contributions. Both components exhibit increasing magnetization with decreasing temperature. Since Bloch's law describes the thermal demagnetization arising from spin-wave excitations in ferro(ferri)magnetic lattices, the analysis was applied only to the ferrite component. The temperature dependence of M_s^{ferrite} is well described by the progressive suppression of thermally excited spin waves with decreasing temperature, leading to improved alignment of magnetic moments within the ferrite lattice. Accordingly, the temperature dependence of the ferrite saturation magnetization was analyzed using Bloch's law [12]:

$$M_s^{\text{ferrite}}(T) = M_s^{\text{ferrite}}(0)(1 - AT^{3/2}) \quad (7)$$

where $M_s(T)$ is the saturation magnetization at temperature T , $M_s(0)$ is the extrapolated magnetization at 0 K, and A is the Bloch constant associated with thermally induced spin-wave excitations.

As shown in Fig. 7, the experimental $M_s(T)$ data are reasonably well described by Bloch's relation for all investigated compositions, suggesting that spin-wave-related thermal demagnetization remains an important contribution within the investigated temperature range. The extracted Bloch constants are approximately $A \approx 2.31 \times 10^{-5} \text{ K}^{-3/2}$ for $x = 0.3$, $1.35 \times 10^{-5} \text{ K}^{-3/2}$ for $x = 0.5$, and $2.60 \times 10^{-5} \text{ K}^{-3/2}$ for $x = 0.7$, which are comparable to previously reported values for spinel ferrites [12]. The variation of the Bloch constant with Mn content indicates that cation substitution modifies the thermal magnetic response of the ferrite lattice, reflecting changes in the effective magnetic exchange interactions and spin-wave stiffness. In particular, the comparatively lower A value for $x = 0.5$ suggests a slower thermal demagnetization rate, implying a relatively greater tability of spin alignment against thermal fluctuations within this composition.

To further evaluate the role of anisotropy and interparticle interactions, the squareness ratio $R = M_r/M_s^{\text{total}}$ was evaluated as a function

of temperature (Table 3). Between 55 K and 150 K, the $x = 0.3$ and $x = 0.5$ samples exhibit $R \approx 0.5$, which is broadly consistent with the behavior expected for randomly oriented assemblies of single-domain particles within the Stoner-Wohlfarth approximation [36]. As the temperature increases, the squareness ratio decreases progressively, indicating that thermal activation increasingly influences the magnetization reversal process by reducing the remanent magnetization and promoting deviations from ideal coherent rotation. At 300 K, the squareness ratio decreases to approximately $R \approx 0.3$, reflecting a thermally softened magnetic state. Nevertheless, the finite coercivity observed at room temperature indicates that the nanoparticles remain magnetically blocked throughout the investigated temperature range and do not exhibit fully developed superparamagnetic behavior [37].

In contrast, the $x = 0.7$ sample exhibits comparatively larger squareness ratios, decreasing from approximately $R \sim 0.75$ at 55 K to $R \sim 0.4$ at 300 K. This distinct behavior indicates a different magnetization reversal mechanism compared with the $x = 0.3$ and $x = 0.5$ samples. The difference is consistent with the structural evolution revealed by XRD, Raman spectroscopy, and TEM analyses, particularly the disappearance of the $\alpha\text{-Fe}$ secondary phase together with the reduction in crystallite size and the establishment of a more homogeneous spinel ferrite structure. These structural modifications are expected to alter the effective magnetic interactions within the nanoparticle assembly and consequently influence the magnetization reversal process. Their specific contributions are discussed further in the subsequent analysis of effective anisotropy and interparticle interactions.

To further examine the magnetization reversal behavior, the temperature dependence of coercivity was analyzed using Kneller's relation [36]:

$$H_c(T) = H_c(0)[1 - (T/T_B)^{1/2}], \quad (8)$$

where $H_c(0)$ is the extrapolated coercivity at 0 K and T_B is the fitting parameter associated with the thermally activated coercivity model. It should be noted that Kneller's relation is applied here primarily to evaluate the applicability of the thermally activated coercivity model within the measured temperature range, rather than to determine the blocking temperature quantitatively.

As shown in Fig. 8, the $x = 0.3$ and $x = 0.5$ samples exhibit reasonably good agreement with Kneller's scaling relation over the experimentally accessible temperature range (55–300 K), suggesting that the temperature dependence of coercivity is broadly consistent with thermally activated magnetization reversal governed by effective energy barriers governing thermally activated magnetization reversal. In contrast, the $x = 0.7$ sample exhibits a noticeable deviation from the predicted scaling behavior, indicating that the simple Kneller model does not fully describe the coercivity evolution for this composition. Such deviation suggests that additional factors beyond the ideal thermally activated reversal model contribute to the magnetization reversal process. These factors may include the reduced crystallite size, enhanced surface-

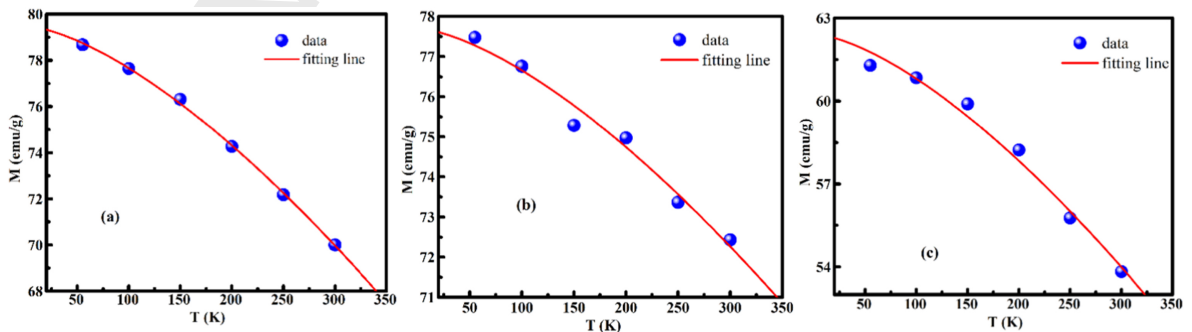


Fig. 7. Temperature dependence of the saturation magnetization $M_s^{\text{ferrite}}(T)$ for $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs with (a) $x = 0.3$, (b) $x = 0.5$, and (c) $x = 0.7$. The solid lines represent the best fits according to Bloch's $T^{3/2}$ law [Eq. (7)], used to estimate the extrapolated zero-temperature saturation magnetization $M_s(0)$ and the Bloch constant A associated with spin-wave excitations.

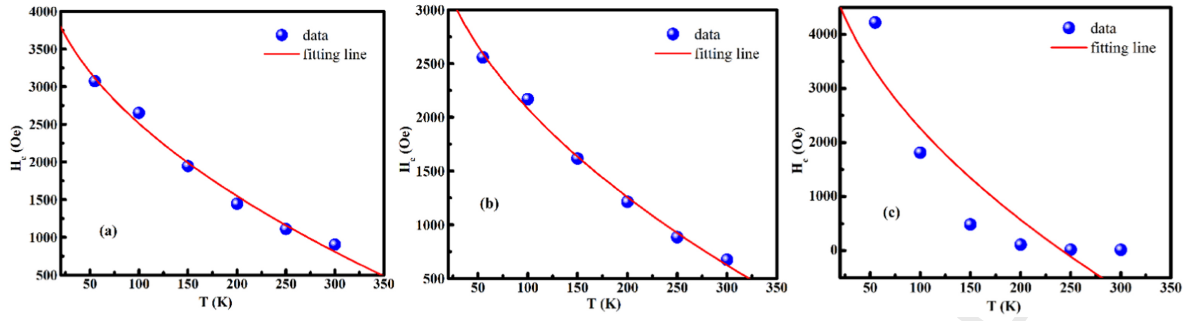


Fig. 8. Temperature dependence of coercivity H_c for $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs with (a) $x = 0.3$, (b) $x = 0.5$, and (c) $x = 0.7$. The solid lines in panels (a) and (b) represent the best fits according to Kneller's relation [Eq. (8)]. In contrast, the $x = 0.7$ sample deviates from the Kneller model, indicating a more complex magnetic reversal behavior associated with enhanced interaction and disorder effects.

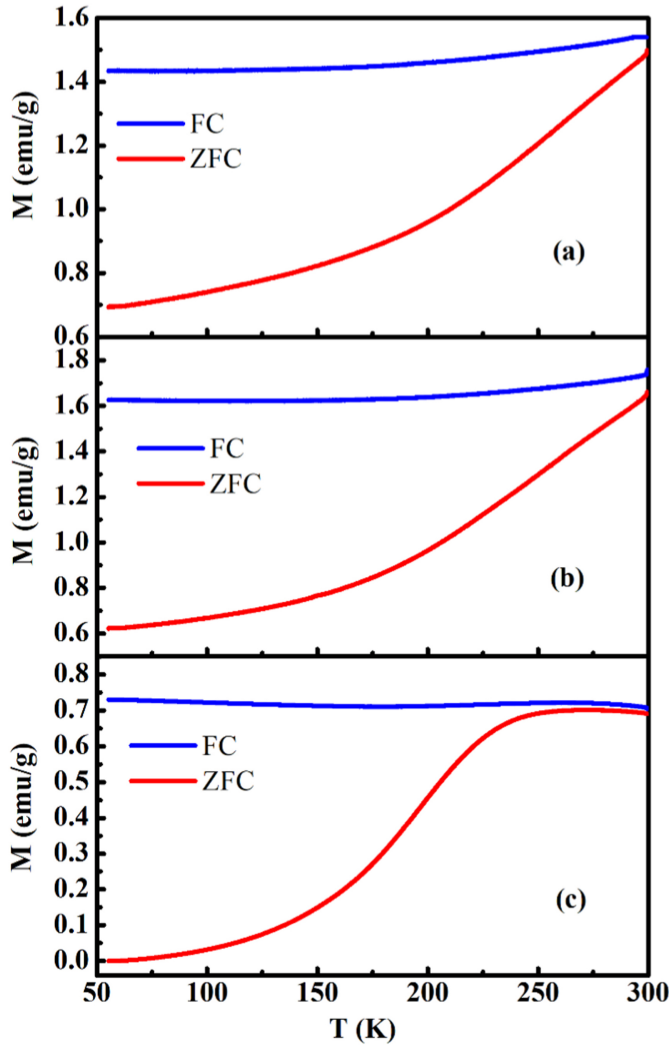


Fig. 9. Field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ nanoparticles for (a) $x = 0.3$, (b) $x = 0.5$, and (c) $x = 0.7$ measured under an applied magnetic field of 100 Oe.

related effects, and changes in interparticle magnetic interactions associated with the more homogeneous nanoparticle assembly. Consequently, the effective energy barriers governing magnetization reversal become more broadly distributed, leading to deviations from the simple Kneller description.

Fig. 9 presents the FC and ZFC magnetization curves, providing complementary information on the temperature-dependent magnetic

relaxation behavior of the nanoparticles. For the $x = 0.7$ sample, the ZFC curve exhibits a well-defined maximum below room temperature, with the peak position corresponding to a blocking temperature of ($T_B = 272.2$) K. Above this temperature, the progressive decrease in FC/ZFC irreversibility indicates enhanced thermal activation of magnetic relaxation, leading to the transition from a blocked to a thermally fluctuating magnetic state. By contrast, the $x = 0.3$ and $x = 0.5$ samples exhibit persistent FC/ZFC irreversibility throughout the investigated temperature range without convergence up to 300 K, indicating that the magnetic blocking temperature exceeds the maximum measurement temperature of 300 K. This behavior indicates that thermal activation is insufficient to overcome the effective energy barriers governing magnetization reversal within the investigated temperature range. The persistence of magnetic blocking throughout the entire fitting interval is also consistent with the applicability of Kneller's relation for these two compositions. Accordingly, the T_B values obtained from Kneller fitting should be regarded as model-derived fitting parameters rather than experimentally determined blocking temperatures.

The distinct FC/ZFC behavior observed for the $x = 0.3$ and $x = 0.5$ samples is consistent with the composition-dependent structural heterogeneity identified by the XRD/Rietveld refinement, Raman spectroscopy, and magnetic analyses. The coexistence of the spinel ferrite matrix and the minor α -Fe phase is expected to produce spatial variations in magnetic anisotropy and local magnetic environments, thereby giving rise to a distribution of effective energy barriers for thermally activated magnetization reversal.

The present FC/ZFC results are not interpreted as evidence of a spin-glass state because complementary dynamic magnetic measurements, such as frequency-dependent AC susceptibility, were not performed. Nevertheless, the observed behavior is consistent with that commonly reported for magnetically heterogeneous nanoparticle assemblies exhibiting broad distributions of magnetic energy barriers [38–40].

Overall, the combined analyses based on Bloch's law, the law of approach to saturation, Kneller scaling, and FC/ZFC magnetization consistently demonstrate a composition-dependent evolution of the magnetic behavior of the $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ NPs. The $x = 0.3$ and $x = 0.5$ samples are characterized by a strongly blocked magnetic state associated with structural heterogeneity arising from the coexistence of the spinel ferrite matrix and the minor α -Fe phase, whereas the $x = 0.7$ sample exhibits a comparatively more homogeneous magnetic response together with enhanced thermal activation. These results establish the experimental basis for the subsequent quantitative analysis of magnetic interactions and magnetization reversal mechanisms presented in the following section.

To further characterize the magnetic reversal volume of the single-phase ferrite $x = 0.7$ sample, the effective magnetic volume (V_m) was estimated at different temperatures using the Néel-Brown relation $K_{eff}V_m = 25k_B T_B$, where k_B is the Boltzmann constant and T_B is the blocking temperature determined from the maximum of the ZFC magnetization curve. The experimentally determined T_B of 272.2 K was subsequently used to estimate V_m , which was further applied for evaluating

the magnetic diameter and dipolar interaction field. [40]. The relation $K_{eff} = H_c M_s / 0.64$ has been widely employed as a first-order approximation for randomly oriented single-domain nanoparticles with approximately spherical morphology and cubic anisotropy [38–40]. It should be emphasized that this procedure is used solely to estimate the effective magnetic reversal volume and does not constitute independent evidence of interparticle interactions. The corresponding magnetic diameters (D_m) calculated from V_m are summarized in Table 4.

The estimated magnetic diameter exhibits a systematic increase with increasing temperature. At 55 K, the estimated magnetic diameter remains smaller than the physical particle size measured by TEM ($D_{TEM} \approx 10.3$ nm), volume effectively participates in coherent magnetization reversal. Such behavior is commonly attributed to magnetically disordered surface spins or magnetically inactive regions surrounding a magnetically ordered core, as frequently observed in ferrite nanoparticles. As the temperature increases, the estimated magnetic diameter gradually approaches the physical particle size, suggesting that the effective magnetic reversal volume progressively increases with temperature.

To qualitatively evaluate the influence of surface magnetic disorder, the relative volumes of the magnetically ordered core and the magnetically disordered surface region were estimated from the difference between D_m and D_{TEM} . At 55 K, the calculated surface contribution is appreciable, indicating that surface spin disorder and broken exchange symmetry at the nanoparticle boundaries may contribute significantly to the effective magnetic anisotropy and coercive behavior of the $x = 0.7$ sample. These results further support the important role of surface effects in governing the low-temperature magnetic response of the present nanoparticles.

The maximum nearest-neighbor dipolar field was subsequently estimated using $H_{dip} = 2\mu/d^3$, where $\mu = M_s V_m$ is the magnetic moment of

Table 4

Temperature-dependent magnetic parameters of the $x = 0.7$ sample, including the effective anisotropy constant (K_{eff}), estimated dipolar interaction field (H_{dip}) and magnetic diameter (D_m).

Temp. (K)	$K_{eff} \times 10^5$ (erg/cm ³)	H_{dip} (kOe)	D_m (nm)
55	21.34(5)	0.25(9)	9.4(4)
100	9.08(7)	0.60(3)	12.5(5)
150	2.39(4)	2.25(4)	19.5(7)
200	0.52(8)	9.93(8)	32.4(0)
250	0.07(6)	66.16(7)	61.8(3)
300	0.05(9)	81.40(3)	67.0(4)

an individual particle [40,41]. Following the assumption adopted by Xu et al. [40], the nanoparticles were approximated as spherical and the center-to-center distance (d) between two nearest-neighbor particles was taken as the physical particle diameter determined from TEM, corresponding to particles in direct contact. Under this assumption, the calculated H_{dip} values increase progressively with temperature (Table 4). This increase originates directly from the increase in the effective magnetic moment associated with the larger magnetic reversal volume. Accordingly, the calculations suggest that dipolar interactions become progressively more relevant as the effective magnetic volume increases.

The increase in the estimated dipolar interaction field is consistent with the magnetic behavior discussed above. In particular, it provides a plausible explanation for the progressive reduction of the squareness ratio (M_r/M_s) with increasing temperature and for the deviation of the $x = 0.7$ sample from the classical Kneller scaling relation. Together with the relatively small coercivity observed above approximately 150 K, these results indicate that magnetization reversal is increasingly influenced by thermally activated relaxation in combination with interparticle interactions, rather than solely by intrinsic magnetocrystalline anisotropy.

The FC/ZFC measurements provide additional support for this interpretation. As discussed previously, the $x = 0.7$ sample exhibits a well-defined blocking temperature below room temperature together with a progressive reduction of FC/ZFC irreversibility as the temperature increases, reflecting the onset of thermally activated magnetic relaxation. Considering the comparatively small coercivity at elevated temperatures, the nanoscale particle size determined by TEM, and the increasing dipolar interaction field estimated above, the magnetic behavior of the $x = 0.7$ sample is more appropriately described as approaching an interacting-superparamagnetic-like (ISPM-like) regime rather than an ideal assembly of non-interacting superparamagnetic nanoparticles.

To further evaluate this interpretation, the magnetization isotherms were analyzed using both the classical and modified Langevin scaling approaches. As shown in Fig. 10(a), the conventional M/M_s versus H/T scaling fails to produce a universal collapse of the magnetization curves measured between 150 and 300 K, indicating that the classical non-interacting superparamagnetic description is inadequate for the present system. Such deviations have frequently been reported for nanoparticle assemblies in which interparticle interactions influence the magnetic response [43].

Following the modified Langevin model proposed by Allia et al. [43], interaction effects can be incorporated through an effective interaction temperature (T^*), which is related to the dipolar interaction energy by $\varepsilon_D = k_B T^*$. The corresponding magnetization is expressed as

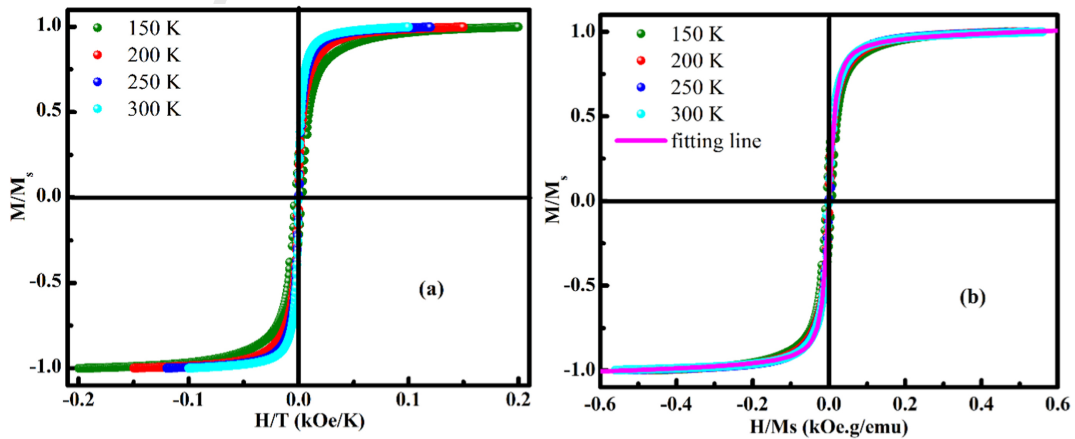


Fig. 10. Superparamagnetic scaling analysis of the $x = 0.7$ sample in the temperature range 150–300 K: (a) normalized magnetization curves plotted as M/M_s versus H/T showing the breakdown of classical Langevin scaling due to interparticle interactions; (b) modified scaling plots of M/M_s versus H/M_s where the isotherms collapse onto a common master curve, consistent with an interacting superparamagnetic (ISPM) state described by the modified Langevin model.

$$M = N\mu L\left[\frac{\mu H}{k_B(T + T^*)}\right] \quad (9)$$

where $L(x)$ is the Langevin function.

As shown in Fig. 10(b), the magnetization curves collapse much more closely onto a common master curve when plotted using the modified Langevin scaling approach. The fitting yields an effective interaction temperature of approximately $T^* \approx 84$ K, corresponding to a dipolar interaction energy of $\varepsilon_D = k_B T^* \approx 7.24 \times 10^{-3}$ eV. This interaction energy is comparable to values reported for interacting ferrite nanoparticle assemblies, including Fe_3O_4 - and MnFe_2O_4 -based systems [12,43], providing additional support for the presence of non-negligible dipolar interactions in the present nanoparticles.

Overall, the combined analyses based on the Néel-Brown model, magnetic diameter estimation, dipolar field calculation, FC/ZFC magnetization, Kneller scaling, and modified Langevin analysis consistently indicate that the magnetic response of the $x = 0.7$ sample cannot be adequately described by a non-interacting particle model. Instead, the results support a thermally activated magnetic state in which surface spin disorder and interparticle dipolar interactions jointly influence the effective magnetic anisotropy and magnetization reversal process. This interpretation is fully consistent with the single-phase spinel structure revealed by XRD/Rietveld refinement and provides a coherent explanation for the distinct magnetic behavior of the $x = 0.7$ composition relative to the Fe-containing samples.

4. Conclusions

$\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ nanoparticles ($x = 0.3, 0.5$, and 0.7) were successfully synthesized by the thermal decomposition method, and their structural and magnetic evolution with Mn substitution was systematically investigated. XRD combined with Rietveld refinement revealed the coexistence of spinel ferrite and a minor metallic α -Fe phase in the $x = 0.3$ and $x = 0.5$ samples, whereas the $x = 0.7$ composition exhibited a single-phase spinel structure within the instrumental detection limit. Raman spectroscopy, TEM, and EDX analyses further confirmed composition-dependent local structural variations and nanoscale homogeneity, supporting the structural evolution identified by XRD.

Mn substitution markedly influences both the structural characteristics and magnetic behavior of the nanoparticles. Increasing Mn content suppresses the formation of the α -Fe secondary phase, reduces the crystallite size, and increases lattice microstrain, leading to a progressive transition from a structurally heterogeneous ferrite/ α -Fe system to a structurally homogeneous spinel ferrite. The coexistence of ferrite and α -Fe phases in the $x = 0.3$ and $x = 0.5$ samples provides a consistent explanation for the observed constricted hysteresis loops, whereas the single-phase $x = 0.7$ sample exhibits magnetic behavior dominated by thermally activated relaxation.

Quantitative analyses based on the law of approach to saturation, the Néel-Brown model, dipolar field estimation, FC/ZFC magnetization, Kneller scaling, and modified Langevin analysis demonstrate that the magnetic response evolves systematically with composition. In particular, the $x = 0.7$ sample exhibits characteristics of an interacting-superparamagnetic-like (ISPM-like) regime at elevated temperatures, where surface spin disorder and interparticle dipolar interactions significantly influence magnetization reversal. In contrast, the $x = 0.3$ and $x = 0.5$ samples remain in a strongly blocked magnetic state because of their larger effective anisotropy barriers and structural heterogeneity.

Overall, this work establishes a coherent correlation between phase evolution, structural heterogeneity, and magnetic reversal behavior in Mn-substituted cobalt ferrite nanoparticles synthesized by thermal decomposition. The results demonstrate that controlling Mn concentration provides an effective strategy for tailoring the balance between magnetocrystalline anisotropy, exchange interactions, and dipolar coupling, thereby offering useful guidelines for the design of ferrite nanoparticles with tunable magnetic properties.

CRediT authorship contribution statement

Truong-Tho Nguyen: Writing – original draft, Resources, Project administration, Formal analysis, Data curation. **Tran Thi Ngoc Nha:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Dang Ngoc Toan:** Writing – review & editing, Visualization, Validation, Software, Methodology, Investigation. **Dinh Thanh Khan:** Visualization, Validation, Methodology, Data curation, Conceptualization. **Le Thi Tuyet Ngan:** Validation, Resources, Project administration, Methodology, Investigation, Data curation. **Tran Dang Thanh:** Writing – review & editing, Resources, Methodology, Investigation, Conceptualization. **Do Hung Manh:** Writing – original draft, Formal analysis, Data curation, Conceptualization. **Pham Thanh Phong:** Writing – review & editing, Supervision, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare no conflict of interest.

Acknowledgements

The work was funded by the Vietnam Ministry of Education and Training under the Grant No. B2026-DHH-03.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ceramint.2026.09.139>.

References

- [1] H.M.K. Tedjiekeng, P.K. Tsoabang, R.L. Fomekong, E.P. Etape, P.A. Joy, A. Delcorte, J.N. Lambi, Structural characterization and magnetic properties of undoped and copper-doped cobalt ferrite nanoparticles prepared by the octanoate coprecipitation route at very low dopant concentrations, *RSC Adv.* 8 (2018) 38621, <https://doi.org/10.1039/C8RA08532C>.
- [2] P. Hu, T. Chang, W.-J. Chen, J. Deng, S.-L. Li, Y.-G. Zuo, L. Kang, F. Yang, M. Hostetter, A.A. Volinsky, Temperature effects on magnetic properties of Fe_3O_4 nanoparticles synthesized by the sol-gel explosion-assisted method, *J. Alloys Compd.* 773 (2019) 605, <https://doi.org/10.1016/j.jallcom.2018.09.238>.
- [3] M.P. Ghosh, S. Datta, R. Sharma, K. Tanbir, M. Kar, S. Mukherjee, Copper doped nickel ferrite nanoparticles: Jahn-Teller distortion and its effect on microstructural, magnetic and electronic properties, *Mater. Sci. Eng. B* 263 (2021) 114864, <https://doi.org/10.1016/j.mseb.2020.114864>.
- [4] M. Rashad, D. Rayan, A. Turky, M. Hessien, Effect of Co^{2+} and Y^{3+} ions insertion on the microstructure development and magnetic properties of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ powders synthesized using co-precipitation method, *J. Magn. Mater.* 374 (2015) 359, <https://doi.org/10.1016/j.jmmm.2014.08.031>.
- [5] H. Mund, B. Ahuja, Structural and magnetic properties of Mg doped cobalt ferrite nano particles prepared by sol-gel method, *Mater. Res. Bull.* 85 (2017) 228, <https://doi.org/10.1016/j.materresbull.2016.09.027>.
- [6] H. Moradmard, S.F. Shayesteh, P. Tohidi, Z. Abbas, M. Khaleghi, Structural, magnetic and dielectric properties of magnesium doped nickel ferrite nanoparticles, *J. Alloys Compd.* 650 (2015) 116, <https://doi.org/10.1016/j.jallcom.2015.07.269>.
- [7] M. Hashim, A. Ahmed, S.A. Ali, S.E. Shirsath, M.M. Ismail, R. Kumar, S. Kumar, S.S. Meena, D. Ravinder, Structural, optical, elastic and magnetic properties of Ce and Dy doped cobalt ferrites, *J. Alloys Compd.* 834 (2020) 155089, <https://doi.org/10.1016/j.jallcom.2020.155089>.
- [8] O.K. Mmlesi, N. Masunga, A. Kuvarega, T.T. Nkambule, B.B. Mamba, K.K. Kefeni, Cobalt ferrite nanoparticles and nanocomposites: photocatalytic, antimicrobial activity and toxicity in water treatment, *Mater. Sci. Semicond. Process.* 123 (2021) 105523, <https://doi.org/10.1016/j.mssp.2020.105523>.
- [9] Y. Lu, M. Yousaf, M.N. Akhtar, A. Noor, M. Akbar, M.A.K. Yousaf Shah, S. Yan, F. Wang, Effect of Gd and Co contents on the microstructural, magneto-optical and electrical characteristics of cobalt ferrite (CoFe_2O_4) nanoparticles, *Ceram. Int.* 48 (2022) 2782, <https://doi.org/10.1016/j.ceramint.2021.10.067>.
- [10] Thi Ngoc Nha Tran, Dang Ngoc Toan, Dinh Thanh Khan, Le Thi Tuyet Ngan, Le Viet Bau, Tran Dang Thanh, Do Hung Manh, Pham Thanh Phong, Nguyen Xuan Phuc, Structure-property relationships of CoFe_2O_4 and MnFe_2O_4 nanoferrites: deep insights into optical and magnetic properties, *Ceram. Int.* 51 (2025) 50091, <https://doi.org/10.1016/j.ceramint.2025.08.244>.
- [11] Luu Huu Nguyen, Thai Thi Que Anh, Ta Ngoc Bach, Nguyen Hoai Nam, Dinh Van Tuan, Le The Tam, Dinh Thi Truong Giang, Phan Thi Hong Tuyet, Do Hung Manh, Pham Thanh Phong, Pham Hong Nam, Role of cation distribution in $\text{CoGd}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles on structure, magnetic properties, and applicability in

- hyperthermia and magnetic resonance imaging, *Mater. Chem. Phys.* 345 (2025) 131274, <https://doi.org/10.1016/j.matchemphys.2025.131274>.
- [12] Tran Thi Ngoc Nha, Sankar Hari Prakash, Selvaraj Mohana Roopan, James Jebaselan Samuel, Ngoc Toan Dang, Dinh Thanh Khan, Do Danh Bich, Dang Thanh Tran, Le Thi Tuyet Ngan, Do Hung Manh, Pham Thanh Phong, Microwave-assisted co-precipitation synthesis of MFe_2O_4 nanoferrites ($\text{M} = \text{Co}$ and Mn) using biogenic coir extract and their physical characterization, *RSC Adv.* 15 (2025) 29571, <https://doi.org/10.1039/D5RA004897D>.
- [13] P. Chandramohan, M.P. Srinivasan, S. Velmurugan, S.V. Narasimhan, Cation distribution and particle size effect on Raman spectrum of CoFe_2O_4 , *J. Solid State Chem.* 184 (2011) 89, <https://doi.org/10.1016/j.jssc.2010.10.019>.
- [14] O.K. Mmesi, N. Masunga, A. Kuvarega, T.T. Nkambule, B.B. Mamba, K.K. Kefeni, Cobalt ferrite nanoparticles and nanocomposites: photocatalytic, antimicrobial activity and toxicity in water treatment, *Mater. Sci. Semicond. Process.* 123 (2021) 105523, <https://doi.org/10.1016/j.mssp.2020.105523>.
- [15] M. Shobana, W. Nam, H. Choe, Yttrium-doped cobalt nanoferrites prepared by sol-gel combustion method and its characterization, *J. Nanosci. Nanotechnol.* 13 (2013) 3535, <https://doi.org/10.1166/jnn.2013.7250>.
- [16] D. Cao, L. Pan, J. Li, X. Cheng, Z. Zhao, J. Xu, Q. Li, X. Wang, S. Li, J. Wang, Investigation on the structures and magnetic properties of carbon or nitrogen doped cobalt ferrite nanoparticles, *Sci. Rep.* 8 (2018) 13644, <https://doi.org/10.1038/s41598-018-28968-9>.
- [17] S.P. Yadav, S.S. Shinde, A.A. Kadam, K.Y. Rajpure, Structural, morphological, dielectric and magnetic properties of Mn substituted cobalt ferrite, *J. Semiconduct.* 34 (2013) 093002, <https://doi.org/10.1088/1674-4926/34/9/093002>.
- [18] M.P. Reddy, X. Zhou, A. Yann, S. Du, Q. Huang, A.M.A. Mohamed, Low temperature hydrothermal synthesis, structural investigation and functional properties of $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1.0$) nanoferrites, *Superlattice. Microsc.* 81 (2015) 233, <https://doi.org/10.1016/j.spmi.2015.02.001>.
- [19] Ali A. Ati, Alyaa H. Abdalsalam, Ali S. Hasan, Thermal, microstructural and magnetic properties of manganese substitution cobalt ferrite prepared via co-precipitation method, *J. Mater. Sci. Mater. Electron.* 32 (2021) 3019, <https://doi.org/10.1007/s10854-020-05053-4>.
- [20] P. Monisha, P. Priyadharshini, S.S. Gomathi, K. Pushpanathan, Influence of Mn dopant on the crystallite size, optical and magnetic behaviour of CoFe_2O_4 magnetic nanoparticles, *J. Phys. Chem. Solid.* 148 (2021) 109654, <https://doi.org/10.1016/j.jpcs.2020.109654>.
- [21] Chao Liu, Xiaowei Wu, Timothy Klemmer, Nisha Shukla, Dieter Weller, Reduction of sintering during annealing of FePt nanoparticles coated with iron oxide, *Chem. Mater.* 17 (2005) 620, <https://doi.org/10.1021/cm0403457>.
- [22] S. Torkian, A. Ghasemi, Energy product enhancement in sufficiently exchange-coupled nanocomposite ferrites, *J. Magn. Magn. Mater.* 469 (2019) 119, <https://doi.org/10.1016/j.jmmm.2018.07.018>.
- [23] S. Hazra, M.K. Patra, S.R. Vadera, N.N. Ghosh, A novel but simple “One-Pot” synthetic route for preparation of $(\text{NiFe}_2\text{O}_4)_x-(\text{BaFe}_{12}\text{O}_{19})_{1-x}$ composites, *J. Am. Ceram. Soc.* 95 (2012) 60, <https://doi.org/10.1111/j.1551-2916.2011.04958.x>.
- [24] S. Ammar, A. Helfen, N. Jouini, F. Fievet, I. Rosenman, F. Villain, P. Molinie, M. Danot, Magnetic properties of ultrafine cobalt ferrite particles synthesized by hydrolysis in a polyol medium, *J. Mater. Chem.* 11 (2001) 186, <https://doi.org/10.1039/B003193N>.
- [25] O. Masalaa, D. Hoffmann, N. Sundaramb, K. Pagea, T. Proffen, G. Lawesc, R. Seshadria, Preparation of magnetic spinel ferrite core/shell nanoparticles: soft ferrites on hard ferrites and vice versa, *Solid State Sci.* 8 (2006) 1015, <https://doi.org/10.1016/j.solidstatesciences.2006.04.014>.
- [26] Thi Ngoc Nha Tran, Dinh Thanh Khan, Dang Ngoc Toan, Dang Thanh Tran, Pham Hoai Linh, Pham Hong Nam, Do Hung Manh, Pham Thanh Phong, Nguyen Xuan Phuc, Comparative magnetothermal and photothermal behavior of CoFe_2O_4 -Ag and Fe_3O_4 -Ag ferrite-plasmonic nanocomposites, *Ceram. Inter.* (2026), <https://doi.org/10.1016/j.ceramint.2026.05.167>. In Press.
- [27] F. Pan, Z.S. Zhang, Magnetic property of the face center cubic iron with different lattice parameter in Fe/Pd multilayers, *Physica B* 293 (2001) 237, [https://doi.org/10.1016/S0921-4526\(00\)00560-3](https://doi.org/10.1016/S0921-4526(00)00560-3).
- [28] Alaa A. Akl, Safwat A. Mahmoud, S.M. AL-Shomar, A.S. Hassanien, Improving microstructural properties and minimizing crystal imperfections of nanocrystalline Cu_2O thin films of different solution molarities for solar cell applications, *Mater. Sci. Semicond. Process.* 74 (2018) 183, <https://doi.org/10.1016/j.mssp.2017.10.007>.
- [29] Tran Thi Ngoc Nha, Pham Hong Nam, Dang Thanh Tran, Pham Thanh Phong, Determination of the crystalline size of hexagonal $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3$) nanoparticles from X-ray diffraction—a comparative study, *RSC Adv.* 13 (2023) 25007, <https://doi.org/10.1039/D3RA004018F>.
- [30] Sergio R.S. Veloso, Sara F. Nereu, Carlos O. Amorim, Vítor S. Amaral, Miguel A. Correa-Duarte, Elisabete M.S. Castanheira, Eco-friendly synthesis of fluorescent cobalt-doped manganese ferrites for thermo-therapeutic applications, *Mater. Today Commun.* 39 (2024) 108822, <https://doi.org/10.1016/j.mtcomm.2024.108822>.
- [31] Jonathan E. Spanier, Richard D. Robinson, Feng Zhang, Siu-Wai Chan, Irving P. Herman, Size-dependent properties of CeO_2 nanoparticles as studied by Raman scattering, *Phys. Rev. B* 64 (2001) 245407, <https://doi.org/10.1103/PhysRevB.64.245407>.
- [32] D.L.A. de Faria, S. Venâncio Silva, M.T. de Oliveira, Raman microspectroscopy of some iron oxides and oxyhydroxides, *J. Raman Spectrosc.* 28 (1997) 873, [https://doi.org/10.1002/\(SICI\)1097-4555\(199711\)28:11<873::AID-JRS177>3.0.CO;2-B](https://doi.org/10.1002/(SICI)1097-4555(199711)28:11<873::AID-JRS177>3.0.CO;2-B).
- [33] B.D. Cullity, C.D. Graham, Introduction to Magnetic Materials, second ed., IEEE press, 2009 <https://doi.org/10.1002/9780470386323>.
- [34] K. Honda, H. Masumoto, S. Kaya, *Sci. Rep. Tohoku Univ.* 17 (1928) 111.
- [35] Sunghyun Yoon, Temperature dependence of magnetic anisotropy constant in cobalt ferrite nanoparticles, *J. Magn. Magn. Mater.* 324 (2012) 2620, <https://doi.org/10.1016/j.jmmm.2012.03.019>.
- [36] E.F. Kneller, F.E. Luborsky, Particle size dependence of coercivity and remanence of single-domain particles, *J. Appl. Phys.* 34 (1963) 656, <https://doi.org/10.1063/1.1729324>.
- [37] S.N. Kane, M. Satalkar, Correlation between magnetic properties and cationic distribution of $\text{Zn}_{0.85-x}\text{Ni}_x\text{Mg}_{0.05}\text{Cu}_{0.1}\text{Fe}_2\text{O}_4$ nano spinel ferrite: effect of Ni doping, *J. Mater. Sci.* 52 (2017) 3467, <https://doi.org/10.1007/s10853-016-0636-7>.
- [38] B.Q. Geng, Y.Q. Man, S.T. Xu, Y.F. Xu, X. Sun, Z.X. Dai, G.H. Zheng, High magnetic performance of cobalt ferrite and anomalous magnetizing behavior of $\text{CoFe}_2\text{O}_4/\text{oxide}$ derived from ferrite, *Ceram. Inter.* 42 (2016) 317, <https://doi.org/10.1016/j.ceramint.2015.08.113>.
- [39] Yuanfeng Xu, Yongqing Ma, Shitao Xu, Ganhong Zheng, Zhenxiang Dai, Diluted and undiluted monodispersed CoFe_2O_4 nanoparticles: the effects of post-annealing on magnetic properties, *J. Mater. Sci.* 50 (2015) 4486, <https://doi.org/10.1007/s10853-015-8997-x>.
- [40] S.T. Xua, Y.Q. Ma, G.H. Zheng, Z.X. Dai, Simultaneous effects of surface spins: rarely large coercivity, high remanence magnetization and jumps in the hysteresis loops observed in CoFe_2O_4 nanoparticles, *Nanoscale* 7 (2015) 6520, <https://doi.org/10.1039/C5NR00582E>.
- [41] Davide Peddis, Federica Orr, Andrea Ardu, Carla Cannas, Anna Musinu, Giorgio Piccaluga, Interparticle interactions and magnetic Anisotropy in cobalt ferrite nanoparticles: influence of molecular coating ü, *Chem. Mater.* 24 (2012) 1062, <https://doi.org/10.1021/cm203280y>.
- [42] S. Laureti, G. Varvaro, A.M. Testa, D. Fiorani, E. Agostinelli, G. Piccaluga, A. Musinu, A. Ardu, D. Peddis, Magnetic interactions in silica coated nanoporous assemblies of CoFe_2O_4 nanoparticles with cubic magnetic anisotropy, *Nanotechnology* 21 (2010) 315701, <https://doi.org/10.1088/0957-4484/21/31/315701>.
- [43] P. Allia, P. Tiberto, M. Coisson, A. Chiolero, F. Celegato, F. Vinai, M. Sangermano, L. Suber, G. Marchegiani, Evidence for magnetic interactions among magnetite nanoparticles dispersed in photoreticulated PEGDA-600 matrix, *J. Nanopart. Res.* 13 (2011) 5615, <https://doi.org/10.1007/s11051-011-0249-7>.