

Effect of Metal Nitrate to Fuel Ratio on the Structural, Morphological, Dielectric, Magnetic and Optical Properties of Cd²⁺-Doped Cobalt Ferrite Nanoparticles

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In this study, Co_{0.7}Cd_{0.3}Fe₂O₄ nanoparticles were synthesized using the sol-gel auto-combustion method by varying the metal nitrate-to-fuel (MN/F) ratio, with dextrose serving as the fuel. X-ray diffraction (XRD) analysis confirmed the formation of a single-phase cubic spinel structure. The lattice parameter initially increased with increasing MN/F ratio and subsequently decreased, whereas the crystallite size estimated using the Scherrer equation remained nearly constant at approximately 31 nm across all compositions. Fourier-transform infrared (FTIR) spectra exhibited characteristic absorption bands in the ranges of 574-548 cm⁻¹ and 437-410 cm⁻¹, corresponding to the metal-oxygen vibrations at the tetrahedral and octahedral sites, respectively. The Debye temperature increased as the MN/F ratio increased from 1:1.2 to 1:2, followed by a subsequent decrease. Field-emission scanning electron microscopy (FE-SEM) images revealed densely packed, predominantly spherical grains with slight agglomeration. Energy-dispersive X-ray spectroscopy (EDS) confirmed the presence of the expected constituent elements, namely cobalt, cadmium, iron, and oxygen. The dielectric properties exhibited an exponential decrease with the logarithm of frequency, with a pronounced dependence on the MN/F ratio. Furthermore, the optical band gap increased slightly from 1.78 to 1.83 eV. The saturation magnetization and related magnetic parameters increased with the MN/F ratio. These results establish the role of fuel content in modulating the structural, dielectric, optical and magnetic characteristics of Co_{0.7}Cd_{0.3}Fe₂O₄ nanoparticles.

Keywords: Cd doped cobalt ferrite, Dextrose, Metal nitrate, Fuel, XRD, Dielectric, VSM.

INTRODUCTION

In recent years, nanocrystalline ferrites have attracted considerable attention due to their unique combination of electrical insulating and magnetic properties, which makes them promising materials for various technological applications [1]. Iron oxide is the principal component of ferrites and plays a crucial role in determining their magnetic and electrical characteristics [2]. Ferrites are magnetic materials composed of iron oxide combined with metal or rare-earth oxides. Based on their crystal structures, they are classified into three major groups: spinel, garnet and hexagonal ferrites [3]. Each group exhibits distinct magnetic and electrical properties suitable for different applications [4]. Among them, spinel ferrites have been extensively investigated owing to their versatile properties and broad application potential. They generally possess

the chemical formula AB₂O₄, where A and B represent divalent and trivalent metal cations, respectively. Their crystal structure contains tetrahedral (A) and octahedral (B) sites, which can accommodate different cations and provide opportunities to tailor their properties. These characteristics make spinel ferrites suitable for electronic, electrical, magnetic and high-frequency devices [5,6].

Nanotechnology focuses on materials with dimensions typically ranging from 1 to 100 nm [7]. Such materials can be produced using top-down and bottom-up approaches and often exhibit properties that differ considerably from those of their bulk counterparts [8,9]. The growing interest in the spinel ferrite nanoparticles from their large specific surface area, nanoscale particle size, excellent chemical stability, high reactivity, potential biocompatibility, reusability and distinctive magnetic and electrical characteristics [10]. These

distinctive characteristics have facilitated the exploration of spinel ferrite nanoparticles across diverse fields, encompassing biomedical applications such as magnetic hyperthermia, drug delivery and magnetic resonance imaging (MRI), alongside antibacterial therapy, environmental remediation, data storage, catalysis and hydrogen generation [11,12].

Several wet-chemical approaches have been developed for the synthesis of spinel ferrite nanoparticles such as the sol-gel, chemical co-precipitation and hydrothermal techniques [13]. Their widespread use is attributed to low processing temperatures, relatively low production costs, straightforward experimental procedures and the ability to obtain nanoparticles with desirable quality and satisfactory yields [14]. In particular, the sol-gel auto-combustion technique has been extensively utilized for the preparation of nanomaterials due to its practical advantages and suitability for nanoparticle synthesis [15,16]. Organic fuels such as glycine, citric acid and dextrose facilitate combustion and influence the characteristics of the resulting materials [17]. The phase purity, crystallite size, surface morphology, specific surface area and other physico-chemical properties depend strongly on the fuel type, solution pH and metal nitrate-to-fuel (MN/F) ratio [18-20]. Therefore, careful control of these parameters is therefore essential for tailoring ferrite properties for specific applications.

Cobalt ferrite (CoFe₂O₄) is an important inverse-spinel ferrite known for its high saturation magnetization, high electrical resistivity, relatively narrow band gap and semiconducting characteristics [21-23]. Its structural, dielectric, optical, magnetic and surface properties are strongly influenced by the synthesis method and processing conditions, including pH, fuel type, MN/F ratio and annealing temperature [24,25]. Appropriate control of these parameters enables the modification of cobalt ferrite properties for targeted applications. Cation substitution provides another effective approach to property engineering. Non-magnetic cations such as Zn²⁺ and Cd²⁺ can alter cation distribution between the tetrahedral and octahedral sites, thereby modifying the structural, electrical, and magnetic behaviour of cobalt ferrite [26-28].

Several studies have investigated the synthesis, doping, and property modification of cobalt ferrite nanoparticles. *S. Silva et al.* [29] examined their structural, vibrational and dielectric properties, while *Gomes et al.* [30] reported biogenic synthesis for biomedical applications. *Dhanalakshmi et al.* [31] studied their structural, magnetic, dielectric and impedance characteristics. The effects of Tb [32], Al [33], Cr [34], Zn, Ni and Y doping [35] have also been explored for the photocatalytic, magnetic storage and spintronic applications. Furthermore, *Ahmed et al.* [36] investigated the influence of calcination temperature on crystallite size and material properties, whereas *Salunkhe et al.* [37] examined the effects of the fuel-to-metal-nitrate ratio on morphology, microstructure and crystallite size.

The role of fuel concentration in governing the physico-chemical characteristics of Cd-substituted cobalt ferrite remains insufficiently understood, despite earlier investigations into fuel composition and nitrate-to-fuel ratios in cobalt ferrite systems. To address this research gap, Co_{0.7}Cd_{0.3}Fe₂O₄ nanoparticles were synthesized *via* sol-gel auto-combustion, with dextrose serving as the combustion fuel and the metal nitrate-to-fuel

(MN/F) ratio serving as the principal experimental variable. The influence of the MN/F ratio on crystallographic features, metal-oxygen vibrational modes, surface morphology, dielectric response, optical band gap, and magnetic characteristics was systematically evaluated to elucidate the role of dextrose mediated combustion chemistry in tailoring the physico-chemical properties of Cd-substituted cobalt ferrites.

EXPERIMENTAL

For the preparation of Co_{0.7}Cd_{0.3}Fe₂O₄ nanoparticles, nitrates of cobalt [Co(NO₃)₂·6H₂O], HPLC, India, with purity 99.90%, nitrates of ferric [Fe(NO₃)₃·9H₂O], HPLC, India, purity 99.1%, cadmium nitrate [Cd(NO₃)₂·4H₂O], s d fine Co. Ltd. Purity 99.0%), dextrose [CH₂OH(CHOH)₄CHO], SRL Pvt. Ltd., purity 99.5%, ammonia (25%, HPLC, India) and distilled water were used as starting materials. The nitrates were of AR grade and used as such.

Synthesis: Distilled water was used to dissolve the metal nitrates and the resulting solution was continuously stirred using a magnetic stirrer. Dextrose was then added to the nitrate solution at MN/F ratios of 1:1.2, 1:1.6, 1:2.0 and 1:2.4. The pH of the mixture was adjusted to 7 by adding ammonia solution dropwise. The resulting solution was heated to 80 °C under continuous stirring until a viscous gel formed. The temperature was subsequently increased to 120 °C, initiating self-combustion and producing a fine and ash-like powder. The as-prepared powder was ground using a mortar and pestle and annealed at 750 °C for 4 h. The annealed powders were used for further characterization. The samples prepared at different MN/F ratios of 1:1.2, 1:1.6, 1:2.0 and 1:2.4 were designated as CoDx 1.2, CoDx 1.6, CoDx 2 and CoDx 2.4, respectively.

Characterization: The X-ray diffraction (XRD) patterns were recorded at 300 K using a Rigaku Ultima-IV diffractometer operated at 40 kV and 40 mA with CuK α radiation (λ = 1.5406 Å) over a 2θ range of 20-80°. Fourier transform infrared (FTIR) spectra were acquired at room temperature using a Shimadzu spectrophotometer across the wavenumber range of 4000-400 cm⁻¹. Surface morphology was examined using field-emission scanning electron microscopy (FE-SEM; Carl Zeiss Supra 55, Germany), while elemental composition was assessed by energy-dispersive X-ray spectroscopy (EDS). Diffuse reflectance spectra were recorded using a JASCO V-750 UV-Vis spectrophotometer. Dielectric measurements were performed at 300 K over the frequency range of 100 Hz-1 MHz using an HP 4284A LCR meter. Magnetic hysteresis loops and associated magnetic parameters were measured using a Lakeshore 7410 vibrating sample magnetometer (VSM).

RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis: The room-temperature X-ray diffraction (XRD) patterns of Co_{0.7}Cd_{0.3}Fe₂O₄ nanoparticles prepared at MN/F ratios of 1:1.2, 1:1.6, 1:2.0, and 1:2.4 (CoDx 1.2, CoDx 1.6, CoDx 2, and CoDx 2.4, respectively) are shown in Fig. 1. The diffraction peaks exhibit high intensity and slight broadening, with variations observed among the samples prepared at different MN/F ratios. The

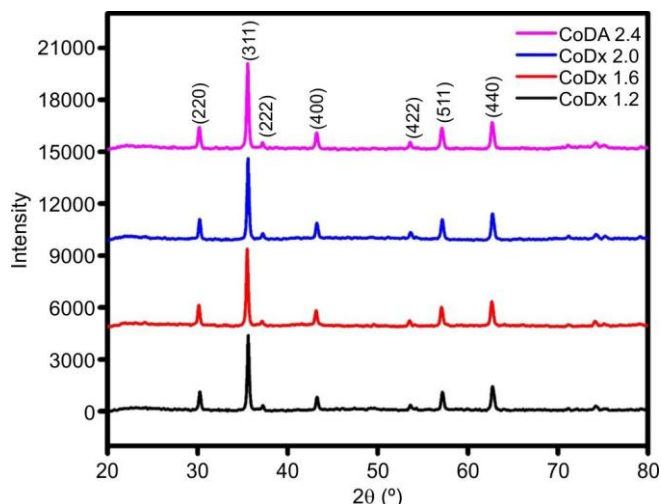


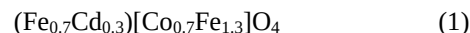
Fig. 1. XRD pattern of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles for varying metal nitrate (MN) to fuel (F) ratio (1:1.2, 1:1.6, 1:2, 1:2.4)

observed reflections were assigned to the (220), (311), (222), (400), (422), (511) and (440) crystallographic planes, which is consistent with the characteristic cubic spinel lattice. The absence of discernible secondary-phase reflections indicates the formation of a single-phase spinel structure within the detection limits of the XRD technique.

The crystallite sizes (t) were estimated using the Scherrer equation [38], and the calculated values are listed in Table-1. The crystallite size remained nearly unchanged across the investigated MN/F ratios. The lattice parameter (a), X-ray density (d_x) and unit-cell volume (V) were calculated using the standard relations [39,40] and are also given in Table-1. These parameters increased as the MN/F ratio increased from 1:1.2 to 1:2.0, followed by a decrease at 1:2.4. The observed variation in lattice parameters may be associated with changes in combustion conditions arising from the MN/F ratio. In solution-combustion synthesis, the fuel-to-oxidizer balance affects the heat released during combustion and consequently, the crystallization process. In addition, the incorporation and distribution of Co^{2+} and Cd^{2+} ions between the tetrahedral (A) and octahedral (B) sites may influence the average metal-oxygen bond lengths and lattice strain. Since Cd^{2+} has a larger ionic radius than Co^{2+} and Fe^{3+} , changes in cation distribution and local structural relaxation may contribute to lattice expansion as the MN/F ratio increases to 1:2.0. At the highest ratio of 1:2.4, the subsequent decrease in lattice parameter may arise from changes in combustion conditions, cation distribution, or residual lattice strain.

Sample code	m.w.	t (nm)	a (Å)	V (Å) ³	d_x (g/cm ³)
CoDx 1.2	250.37	32	8.358	583.94	5.70
CoDx 1.6	250.37	32	8.377	587.81	5.66
CoDx 2.0	250.37	31	8.381	588.61	5.66
CoDx 2.4	250.37	31	8.367	585.79	5.68

Cation distribution: The spinel ferrite lattice possesses (A) and [B] sites, in which cations of varying size and valence can be accommodated as per their site preference energy. Cation distribution influences the various properties of spinel ferrite. According to literature CoFe_2O_4 possesses inverse spinel structure [25,41] whereas cadmium ferrite possesses normal spinel structure [41,42]. Further, Cd has a strong preference towards (A) site. In view of this, the cation distribution of the $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles can be given as:



The above cation distribution is based on the site preference of the elements, no experimental work in this regard is conducted.

FTIR analysis: FTIR spectrum for different metal nitrate (MN) to fuel (F) ratio is shown in Fig. 2, which shows two main absorption bands close to $574\text{--}548\text{ cm}^{-1}$ and $437\text{--}410\text{ cm}^{-1}$. The presence of these two prominent metal-oxygen vibration bands is characteristic of the spinel ferrite structure. The observed absorption bands at around 550 cm^{-1} is attributed to the stretching vibrations of metal ions at (A) site, whereas the band close to 410 cm^{-1} is attributed to stretching vibrations of metal ions at [B] site. The difference between ν_1 and ν_2 originates mainly from the differences in the M–O bond lengths, local coordination environments and corresponding force constants at the (A) and [B] sites. In general, the shorter and relatively stronger M–O bonds at (A) sites give rise to the higher-frequency ν_1 band, whereas the comparatively longer metal-oxygen bonds at octahedral sites produce the lower-frequency ν_2 band.

The values of ν_1 and ν_2 for different metal nitrate (MN) to fuel (F) ratio are listed in Table-2. The positions of ν_1 and ν_2 are found to vary with the MN/F ratio. Both vibrational bands exhibit variations with changes in the MN/F ratio. For CoDx 1.2, the ν_1 and ν_2 bands appear at 551 and 418 cm^{-1} , respectively. At an MN/F ratio of 1:1.6, they shift to lower wavenumbers of 549 and 412 cm^{-1} . A distinct shift toward higher wavenumbers occurs in CoDx 2, with the bands appearing at 574 and 437 cm^{-1} . At the highest ratio of 1:2.4, both bands shift back to lower wavenumbers, reaching 548 and 410 cm^{-1} , respectively.

Sample code	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_{avg} (cm ⁻¹)	θ_D (K)
CoDx 1.2	551	418	484	697.59
CoDx 1.6	549	412	480	691.83
CoDx 2.0	574	437	505	727.82
CoDx 2.4	548	410	489	689.67

Using the following relation, the Debye temperature (θ_D) was calculated [43,44]:

$$\theta_D = \frac{hc}{k_B} \left(\frac{\nu_1 + \nu_2}{2} \right) \quad (2)$$

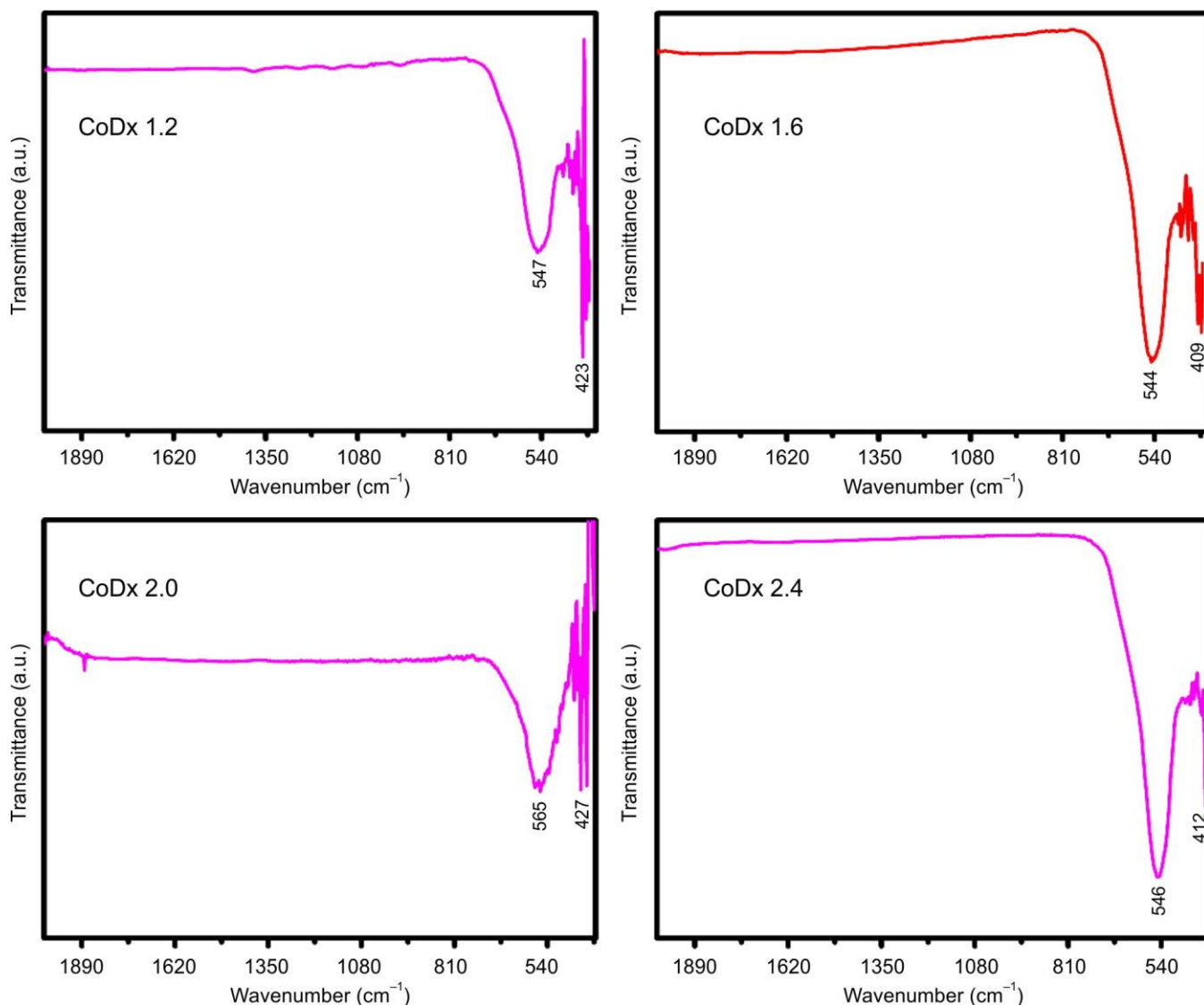


Fig. 2. FTIR spectra of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles for varying metal nitrate (MN) to fuel (F) ratio (1:1.2, 1:1.6, 1:2, 1:2.4)

where, θ_D is Debye temperature in K, h is a Planck's constant (6.626×10^{-34} Js), c is the velocity of light (3×10^8 m/s), k_B is Boltzmann's constant having the value 1.38065×10^{-23} J/K, ν_1 and ν_2 represents the wavenumber of the fundamental absorption bands.

The calculated Debye temperatures are 697.59, 691.83, 727.82 and 689.67 K for CoDx-1.2, CoDx-1.6, CoDx-2.0 and CoDx-2.4, respectively (Table-2). A small decrease in θ_D from 697.59 K for CoDx-1.2 to 691.83 K for CoDx-1.6 is observed, followed by a significant increase to 727.82 K for CoDx-2.0. The Debye temperature subsequently decreases to 689.67 K for CoDx-2.4. Since θ_D is directly related to the characteristic vibrational frequency of the lattice, its variation closely follows the variation in ν_{avg} . The maximum Debye temperature obtained for the CoDx-2.0 sample indicates a higher characteristic phonon frequency and comparatively stronger lattice bonding. Conversely, the lower θ_D of CoDx 2.4 reflects a reduction in the characteristic lattice vibrational frequency, which is consistent with the downward shifts of both ν_1 and ν_2 .

FE-SEM analysis: Fig. 3 presents the FE-SEM images, grain size histograms and EDS spectra of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles, illustrating their surface morphology, grain size distribution and elemental composition. It is observed that the particles exhibit nearly spherical structure with some agglomeration [45,46]. This is due to the high surface energy of NPs and the magnetic dipole-dipole interactions present between ferrite nanoparticles. The grain size measured from distributions indicate average grain sizes of approximately 24.0, 25.30, 27.44 and 26.90 nm for the respective fuel ratios. The grain size initially increases, reaching a maximum at the 1:2.0 ratio, followed by a slight reduction at 1:2.4. This result suggests that the nitrate-to-fuel ratio can influence the morphology. At the 1:2.0 ratio, the combustion conditions may facilitate enhanced crystallite growth and grain development, whereas excess fuel may promote gas evolution and restrict particle growth through the formation of a porous combustion product.

The EDS spectra confirm the existence of cobalt (Co), iron (Fe), cadmium (Cd) and oxygen (O), with no prominent

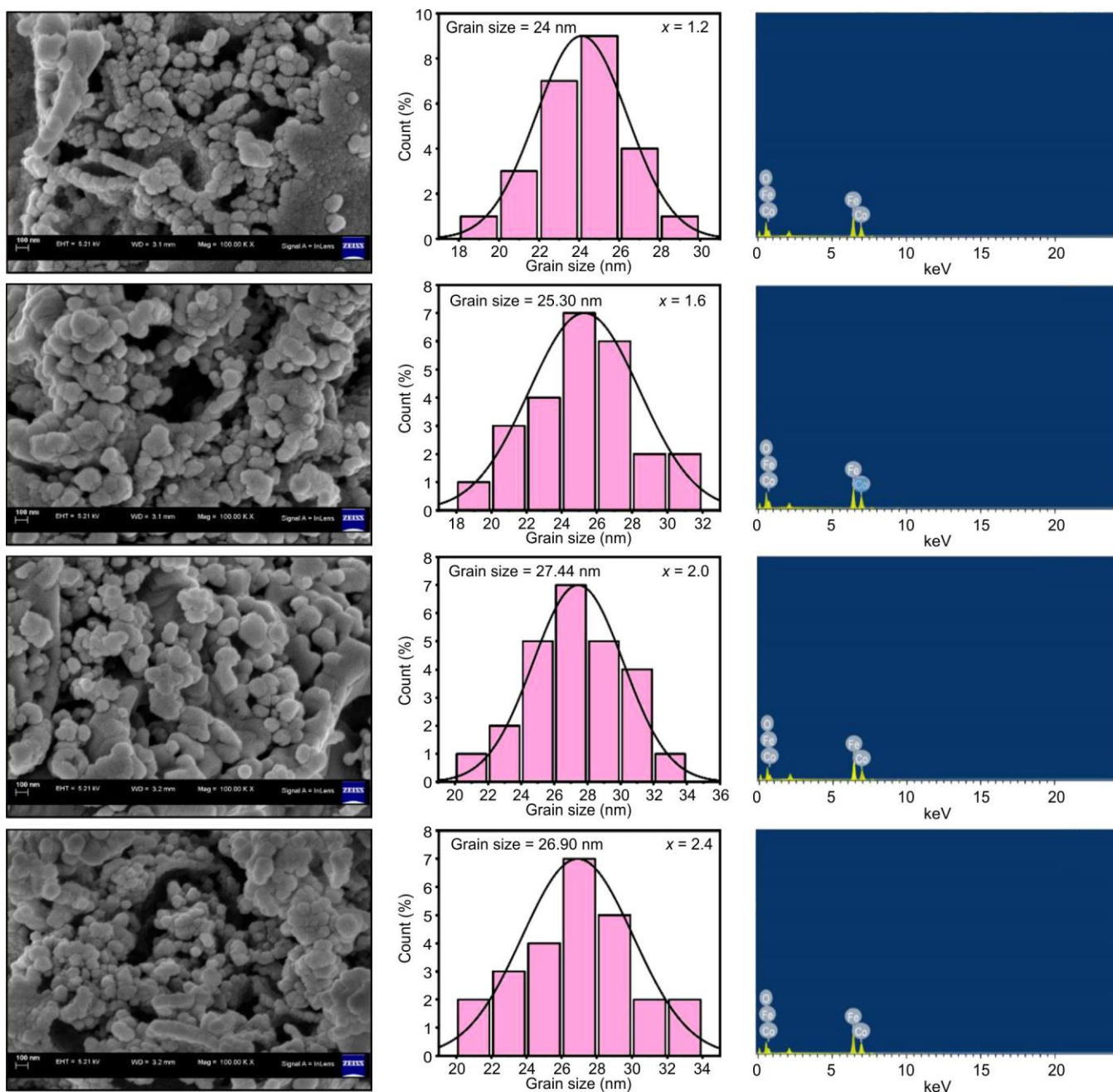


Fig. 3. FE-SEM images, histograms and EDS spectra of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles for varying metal nitrate (MN) to fuel (F) ratio (1:1.2, 1:1.6, 1:2, 1:2.4)

additional elemental peaks are seen in the spectra [47]. The atomic percent (at.%) and weight percent (wt.%) of existing elements are listed in Tables 3 and 4 which is closely agree with that obtained from theoretically. The observed Fe, Co, Cd and O signals support the incorporation of the principal transition-metal constituents into the synthesized ferrite. The absence of additional EDS peaks confirms that no other elements were detected within the measurement limits. Dextrose-assisted combustion provides a simple route for synthesizing $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles, while the MN/F ratio influences grain growth and surface morphology. Among the investigated samples, the MN/F ratio of 1:2.0 yielded the largest average grain size of 27.44 nm.

UV-Visible analysis: The diffuse reflectance spectra of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles prepared at MN/F ratios of 1:1.2, 1:1.6, 1:2.0 and 1:2.4 are shown in Fig. 4. All samples exhibit relatively low reflectance across the measured wavelength range, with a pronounced variation in the UV region near 300 nm and a broad response throughout the visible region. The maximum reflectance decreases from approximately 12% for CoDx 1.2 to below 10% for CoDx 2.4. These changes may be associated with variations in crystallite size, surface morphology, defects and cation distribution arising from differences in combustion conditions. The MN/F ratio can alter combustion kinetics and crystallinity, which affects the interaction of incident light with the nanoparticles and their resulting optical response.

TABLE-3
VALUES OF ATOMIC PERCENTAGE (EXPERIMENTAL AND THEORETICAL) OF CONSTITUENT ELEMENTS OF Co_{0.7}Cd_{0.3}Fe₂O₄ NANOPARTICLES FOR VARYING METAL NITRATE (MN) TO FUEL (F) RATIO (1:1.2, 1:1.6, 1:2, 1:2.4)

Element	CoDx-1.2		CoDx-1.6		CoDx-2.0		CoDx-1.2	
	Expt. (%)	Theo. (%)	Expt. (%)	Theo. (%)	Expt. (%)	Theo. (%)	Expt. (%)	Theo. (%)
Co K	10.42	10.00	10.20	10.0	10.15	10.0	10.16	10.0
Fe K	29.11	28.57	28.32	28.57	28.48	28.57	28.51	28.57
O K	56.34	57.14	57.41	57.14	56.89	57.14	56.94	57.14
Cd	4.12	4.28	4.05	4.28	4.47	4.28	4.39	4.28
Total	99.99	99.99	99.98	99.99	99.99	99.99	100	99.99

TABLE-4
VALUES OF WEIGHT PERCENTAGE (EXPERIMENTAL AND THEORETICAL) OF CONSTITUENT ELEMENTS OF Co_{0.7}Cd_{0.3}Fe₂O₄ NANOPARTICLES FOR VARYING METAL NITRATE (MN) TO FUEL (F) RATIO (1:1.2, 1:1.6, 1:2, 1:2.4)

Element	CoDx-1.2		CoDx-1.6		CoDx-2.0		CoDx-1.2	
	Expt. (%)	Theo. (%)	Expt. (%)	Theo. (%)	Expt. (%)	Theo. (%)	Expt. (%)	Theo. (%)
Co K	16.11	16.45	16.36	16.45	16.41	16.45	16.42	16.45
Fe K	44.38	44.55	44.44	44.55	44.58	44.55	44.52	44.55
O K	25.18	25.53	25.42	25.53	25.56	25.53	25.50	25.53
Cd	13.32	13.45	13.47	13.45	13.44	13.45	13.45	13.45
Total	99.99	99.98	99.69	99.98	99.99	99.98	99.89	99.98

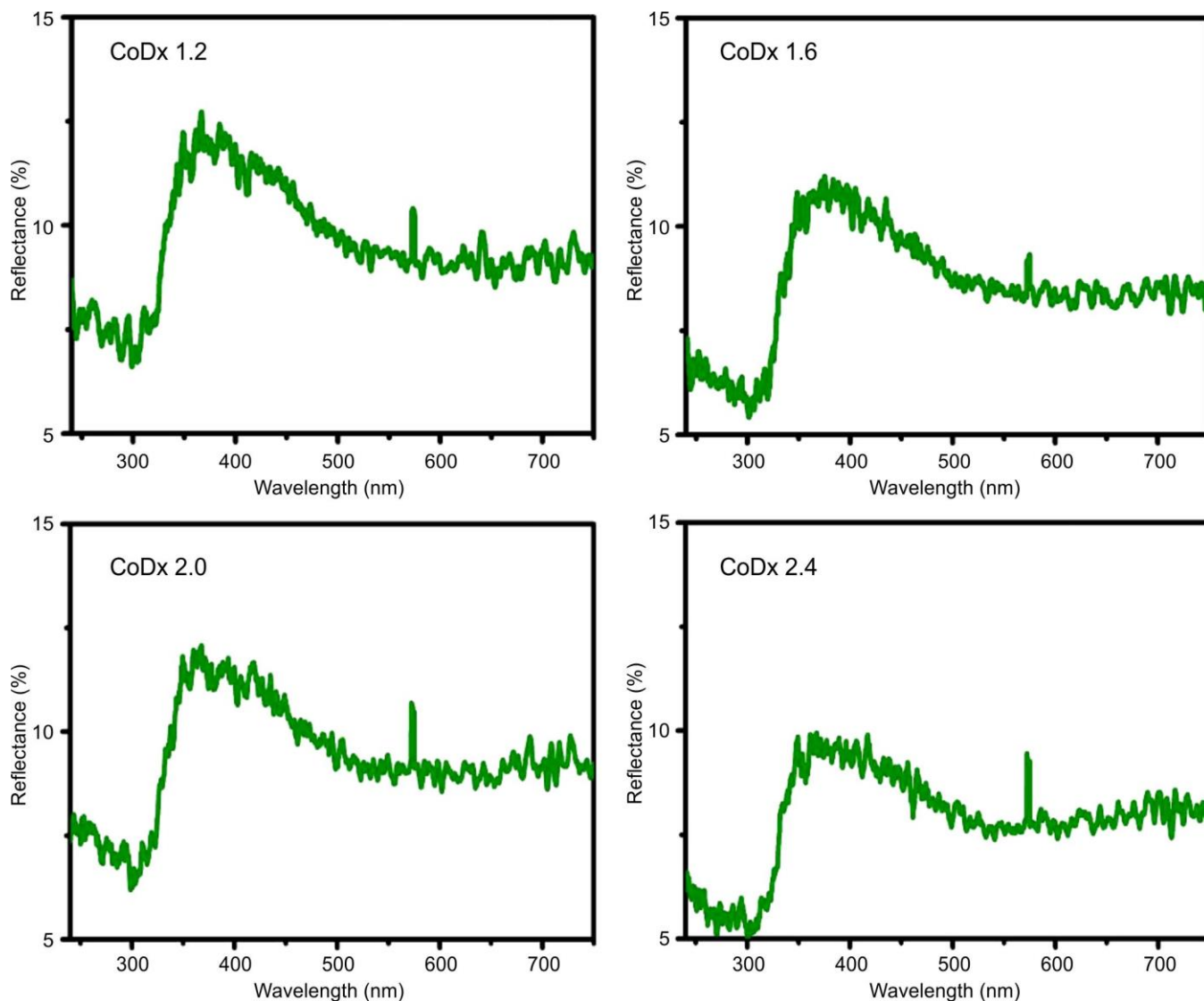


Fig. 4. UV-DRS spectra of Co_{0.7}Cd_{0.3}Fe₂O₄ nanoparticles for varying metal nitrate (MN) to fuel (F) ratio (1:1.2, 1:1.6, 1:2, 1:2.4)

The energy band gap (E_g) was estimated from the Tauc relation [48,49]:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (3)$$

where notations have their usual meaning. Here, n is a constant having values 2 or $1/2$ for allowed direct and indirect transitions respectively. Fig. 5 represents the plot of $(\alpha h\nu)^2$ versus $h\nu$, considering the direct band gap. However, the linearity of this plot alone does not establish the direct-band-gap character of the material and the estimated optical gap depends on the assumed transition model and the selected fitting region. This plot is known as Tauc plot and revealed band-gap energies in the approximate range of 1.78, 1.80, 1.82 and 1.83 eV respectively for CoDx 1.2, CoDx 1.6, CoDx 2 and CoDx 2.4. The band gap energy (E_g) remains nearly unchanged across the investigated MN/F ratios, with only minor variations in the estimated values. The structural changes in the spinel ferrites can alter Fe–O and Co/Cd–O interactions and affect the electronic states near the valence and conduction bands. The small variation in E_g requires

uncertainty analysis of the Tauc plots to assess the reliability of the calculated values.

The relatively narrow optical band gap and broad visible light absorption indicate the potential of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles for visible-light-responsive applications. The UV-DRS and Tauc analyses establish a relationship between the MN/F ratio and the optical properties of the synthesized Co–Cd spinel ferrite nanoparticles.

Dielectric studies: The frequency-dependent dielectric properties of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles synthesized at different MN/F ratios are shown in Figs. 6-8 and the corresponding values are given in Table-5. The dielectric constant (ϵ'), dielectric loss (ϵ'') and loss tangent ($\tan \delta$) vary with the frequency and MN/F ratio.

Fig. 6 illustrates the variation of dielectric constant (ϵ') with the logarithm of frequency. All samples exhibit high dielectric constant values at low frequencies followed by a marked decrease with increasing frequency. This behaviour is commonly explained by the Maxwell-Wagner interfacial polarization mechanism and Koop's phenomenological theory

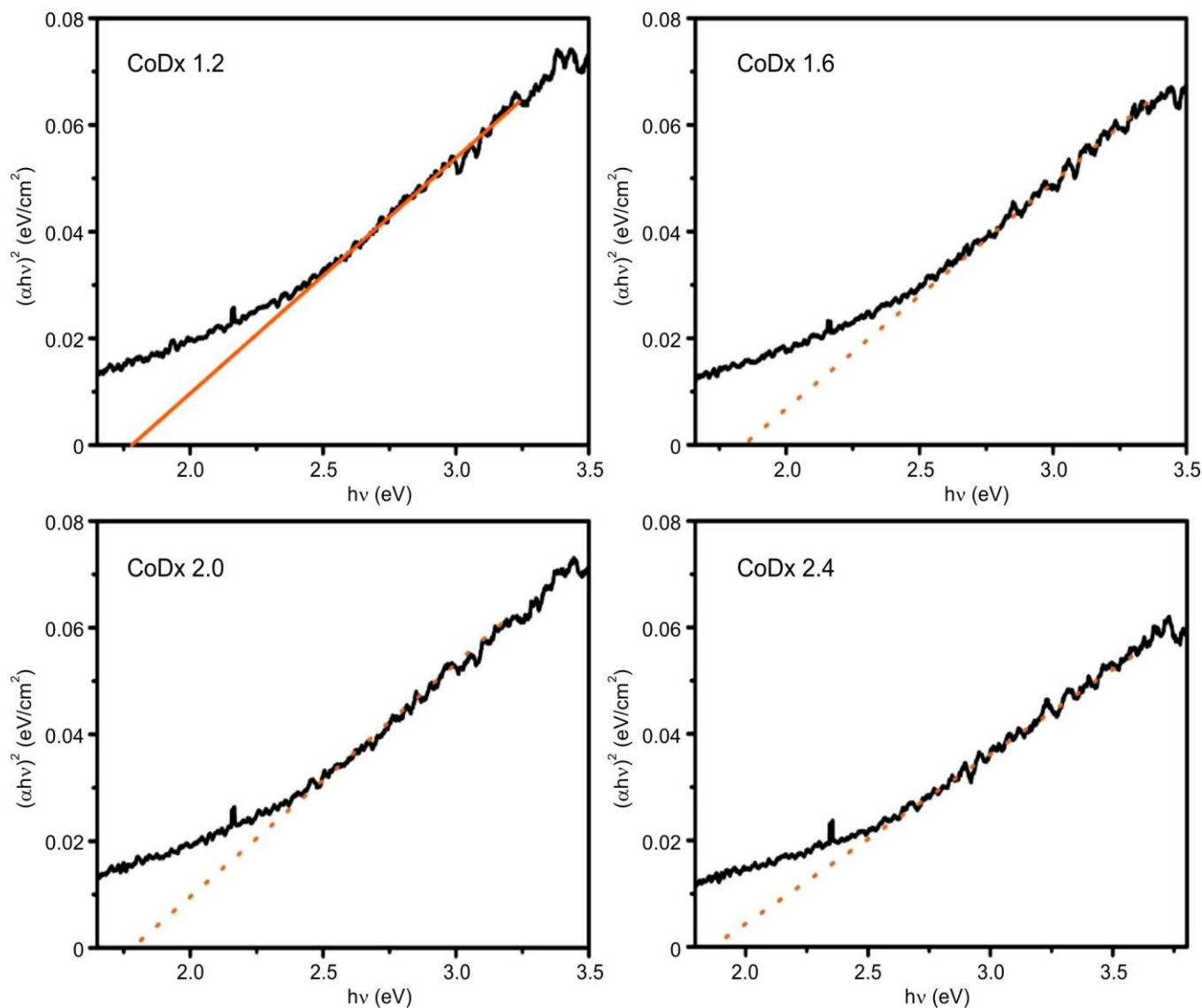


Fig. 5. Tauc plot of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles for varying metal nitrate (MN) to fuel (F) ratio (1:1.2, 1:1.6, 1:2, 1:2.4)

TABLE-5
VALUES OF DIELECTRIC CONSTANT (ϵ'), DIELECTRIC LOSS (ϵ'') AND DIELECTRIC LOSS TANGENT ($\tan \delta$) OF Co_{0.7}Cd_{0.3}Fe₂O₄ NANOPARTICLES FOR VARYING METAL NITRATE (MN) TO FUEL (F) RATIO (1:1.2, 1:1.6, 1:2, 1:2.4)

Sample code	At 50 Hz			At 5 MHz		
	ϵ'	ϵ''	$\tan \delta$	ϵ'	ϵ''	$\tan \delta$
CoDx 1.2	687.27	3962.27	5.76	38.23	2.64	0.06
CoDx 1.6	451.68	1609.59	3.56	38.27	4.42	0.11
CoDx 2.0	704.41	1569.28	2.22	38.24	5.58	0.14
CoDx 2.4	507.26	2173.20	4.28	38.33	2.69	0.07

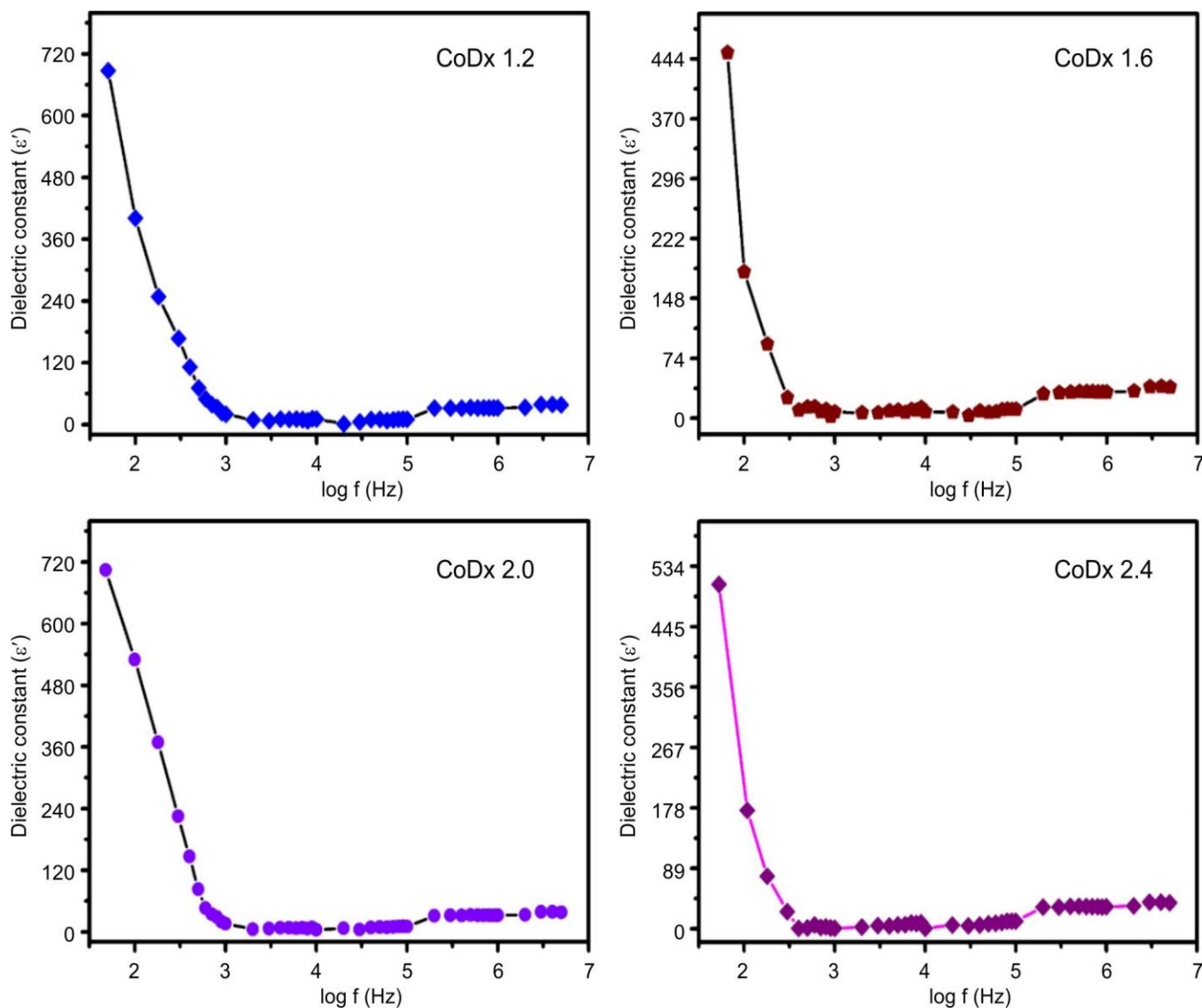


Fig. 6. Variation of dielectric constant of Co_{0.7}Cd_{0.3}Fe₂O₄ nanoparticles with respect to frequency for varying metal nitrate (MN) to fuel (F) ratio (1:1.2, 1:1.6, 1:2, 1:2.4)

[50]. According to this model, ferrites consist of relatively conducting grains separated by highly resistive grain boundaries. At low frequencies, charge carriers accumulate at these interfaces under the applied electric field, giving rise to strong space-charge polarization and high dielectric constant values. Localized charge-carrier hopping between Fe²⁺ and Fe³⁺ ions may contribute to the dielectric response. As the frequency increases, the charge carriers and interfacial polarization become less responsive to the rapidly alternating electric field.

The dielectric constant consequently decreases and approaches a comparatively low value at higher frequencies.

The magnitude of (ϵ') varies with the MN/F ratio. CoDx 2 sample exhibits the highest low-frequency dielectric constant, which is due to the differences in interfacial polarization and charge transport among the samples. Variations in the combustion conditions may alter grain-boundary characteristics, defect concentration and charge-carrier mobility. Although CoDx 2 sample also exhibits the highest FTIR vibrational

frequencies and Debye temperature, but these observations do not establish a direct relationship with its enhanced dielectric constant.

Fig. 7 presents the frequency dependence of dielectric loss (ϵ''). All samples exhibit high dielectric loss at low frequencies followed by a rapid decrease as the frequency increases. At higher frequencies, ϵ'' approaches relatively low values. The magnitude of dielectric loss depends on the MN/F ratio. CoDx 1.2 exhibits the highest low-frequency loss, followed approximately by CoDx 2.4, whereas CoDx 1.6 and CoDx 2 show comparatively lower values. These differences may arise from variations in grain and grain-boundary characteristics, defect concentration, charge-carrier mobility and electrical resistivity. High dielectric loss at low frequencies is associated with greater energy dissipation through charge transport and polarization processes. The decline in ϵ'' at higher frequencies indicates a reduced contribution from slower polarization mechanisms. The different trends in ϵ' and ϵ'' further indicate that a high dielectric constant does not necessarily correspond to high dielectric loss.

Fig. 8 shows the variation of the dielectric loss tangent ($\tan \delta$) with frequency. All samples exhibit relatively high loss tangent values in the low-frequency region, followed by a decrease with increasing frequency. At higher frequencies, $\tan \delta$ becomes comparatively small. The loss tangent also varies with the MN/F ratio. CoDx 1.2 exhibits the highest low frequency ($\tan \delta$), whereas CoDx 2 shows the lowest value. CoDx 1.6 and CoDx 2.4 exhibit intermediate values. These differences may be associated with variations in grain-boundary resistance, defect concentration, charge-carrier mobility and microstructural characteristics arising from the different combustion conditions. The combination of a relatively high dielectric constant and low loss tangent in CoDx 2 indicates a favourable dielectric response within the investigated frequency range. This interpretation remains tentative without further evidence from impedance and microstructural analyses. The low loss tangent values at higher frequencies are consistent with reduced contributions from the interfacial polarization and associated energy-dissipation processes. The observed frequency-dependent dielectric dispersion is

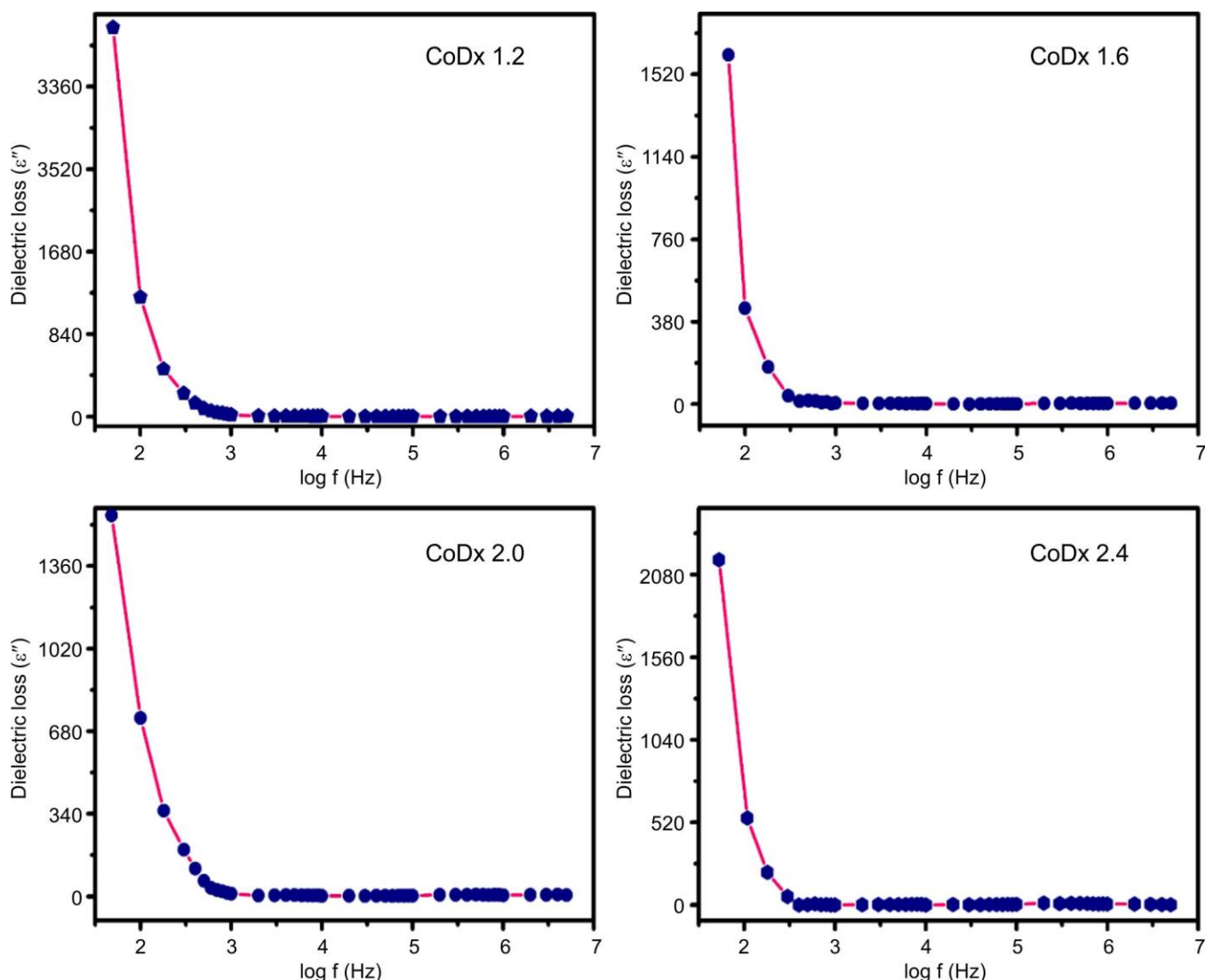


Fig. 7. Variation of dielectric loss of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles with respect to frequency for varying metal nitrate (MN) to fuel (F) ratio (1:1.2, 1:1.6, 1:2, 1:2.4)

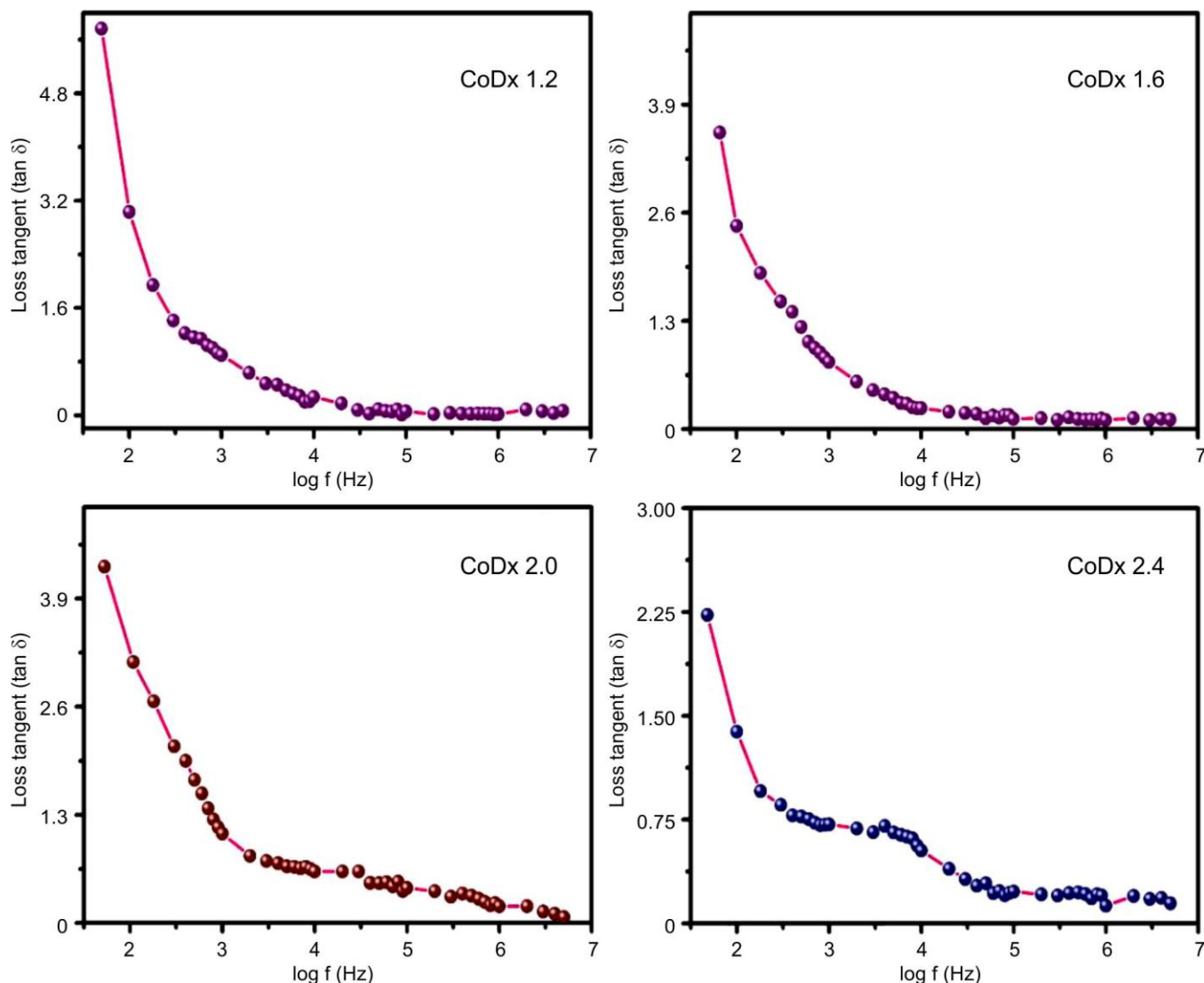


Fig. 8. Variation of loss tangent of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles with respect to frequency for varying metal nitrate (MN) to fuel (F) ratio (1:1.2, 1:1.6, 1:2, 1:2.4)

consistent with interfacial polarization and charge-carrier transport in ferrite nanoparticles. The present measurements alone do not conclusively establish the dominant mechanisms. Impedance spectroscopy would provide further insight into grain and grain-boundary contributions, electrical resistance, and charge-carrier relaxation.

Vibrating sample magnetometer (VSM): Room temperature (300 K) measurements of various magnetic characteristics were performed with the help of VSM technique. The magnetic characteristics of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ NPs were investigated using magnetization (M) vs. applied magnetic field (H) hysteresis measurements. All samples exhibit characteristic S-shaped hysteresis loops (Fig. 9), which indicate the ferri-magnetic behaviour with a tendency toward magnetic saturation at higher applied fields. The saturation magnetization (M_s) increases from approximately 48.98 emu/g for the 1:1.2 ratio to about 63.73 emu/g for 1:1.6, reaching a maximum of approximately 72.73 emu/g for the 1:2.0 ratio. A slight decrease to approximately 70.64 emu/g is observed for the 1:2.4 ratio. The values of M_s for all the samples are shown in Table-6.

The M_s of the samples (CoDx 1:2) is found to be closely matches with the reported values [51]. This variation indicates that the fuel concentration significantly influences the magnetic response of the synthesized ferrite NPs. The enhanced magnetization at the 1:2.0 ratios may be associated with improved crystallinity and the changes in cation distribution arrangement. The subsequent reduction in magnetization at the higher fuel ratio may be related to variations in particle size, surface spin disorder and the development of magnetically disordered surface layers. The values of coercivity (H_c) and remanence (M_r) are also given in Table-6.

The narrow hysteresis loops with small separation between the ascending and descending branches indicate low coercivity and reduced hysteresis loss typical of soft ferrimagnetic materials. At high magnetic fields the magnetization approaches saturation as the magnetic moments progressively align with the applied field. The magnetic response depends on the contributions of Co^{2+} and Fe^{3+} ions and the influence of non-magnetic Cd^{2+} ions on their distribution between the tetrahedral and octahedral sites. The M–H curves show that the MN/F

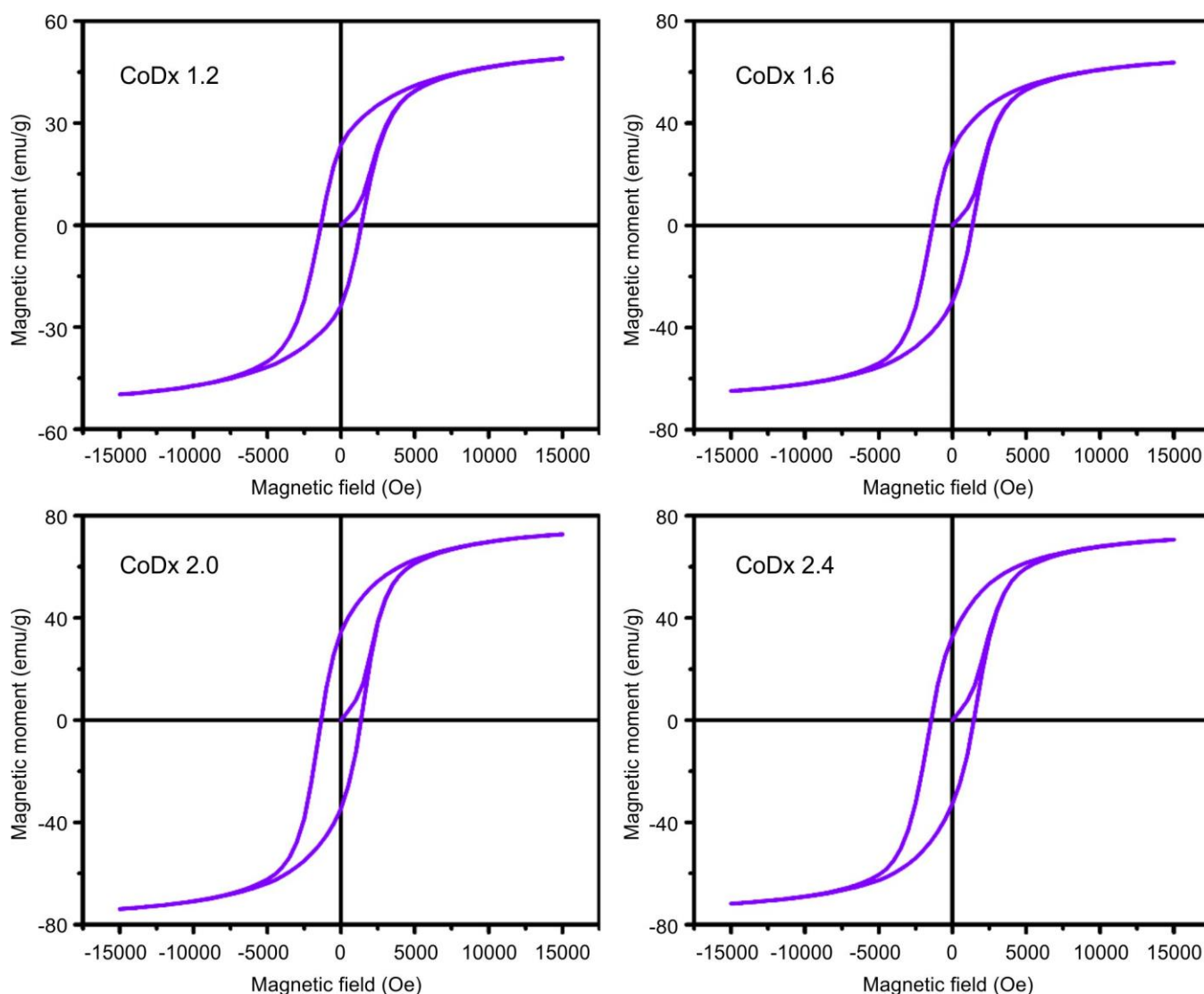


Fig. 9. M-H hysteresis curve of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles for varying metal nitrate (MN) to fuel (F) ratio (1:1.2, 1:1.6, 1:2, 1:2.4)

TABLE-6
VALUES OF SATURATION MAGNETIZATION (M_s), REMANENCE MAGNETIZATION (M_r), COERCIVITY (H_c), REMANENCE RATIO (M_r/M_s), MAGNETON NUMBER (n_B) OF $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ NANOPARTICLES FOR VARYING METAL NITRATE (MN) TO FUEL (F) RATIO (1:1.2, 1:1.6, 1:2, 1:2.4)

Sample code	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	M_r/M_s	n_B (μ_B)	
					Obs.	Cal.
CoDx 1.2	48.98	23.58	1373	0.48	2.197	3.35
CoDx 1.6	63.73	19.72	1347	0.30	2.859	3.35
CoDx 2.0	72.73	34.52	1349	0.47	3.333	3.35
CoDx 2.4	70.64	32.61	1444	0.46	3.169	3.35

ratio influences the magnetic properties of $\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles with the 1:2.0 ratio exhibiting the highest approximate saturation magnetization among the samples.

At high magnetic fields the magnetization approaches saturation as the magnetic moments align progressively with the applied field. The net magnetic moment depends on the contributions of Co^{2+} and Fe^{3+} ions and the redistribution of cations between tetrahedral and octahedral sites. The presence of non-magnetic Cd^{2+} ions may alter the Fe^{3+} distribution and modify the net magnetization. Among the samples studied

$\text{Co}_{0.7}\text{Cd}_{0.3}\text{Fe}_2\text{O}_4$ prepared at an MN/F ratio of 1:2.0 exhibits the highest approximate saturation magnetization.

The magneton number (n_B) is represented as [52]:

$$n_B = \frac{M \times M_s}{5585} \quad (4)$$

where, notations have their usual meaning.

The calculated magneton numbers are listed in Table-6. The magneton number increases with increase in the metal nitrate (MN) to fuel (F) ratio.

The magneton number (n_B^N) was also calculated by applying Neel's model. The magneton number (n_B^N) is represented as [48]:

$$n_B^N = M_B - M_A \quad (5)$$

where notations have their usual meaning. The experimentally observed and theoretically calculated magnetic moment values differ noticeably as shown in Table-6.

Conclusion

Cd(II)-doped cobalt ferrites (Co_{0.7}Cd_{0.3}Fe₂O₄) nanoparticles were synthesized by the sol-gel auto-combustion method using different metal nitrate-to-fuel (MN/F) ratios. XRD analysis confirmed the formation of a single-phase cubic spinel structure. FTIR spectra exhibited two characteristic metal–oxygen absorption bands associated with the spinel structure. FE-SEM images revealed densely packed grains with predominantly spherical morphology, while EDS analysis confirmed the presence of the constituent elements. The optical band gap increased slightly with the MN/F ratio. The dielectric constant and dielectric loss decreased with increasing frequency, with their magnitudes varying among the samples. The M–H curves exhibited ferrimagnetic behaviour and the magnetic parameters depended on the MN/F ratio. The discrepancy between the experimental and calculated magnetic moments may be associated with spin canting and changes in cation distribution. The results establish that the MN/F ratio influences the structural, morphological, vibrational, dielectric, optical and magnetic properties of Co_{0.7}Cd_{0.3}Fe₂O₄ nanoparticles.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

DECLARATION OF AI-ASSISTED TECHNOLOGIES

During the preparation of this manuscript, the authors used an AI-assisted tool(s) to improve the language and no data, results or scientific conclusions were generated by AI. All analyses, interpretations and conclusions are the authors' own. The authors reviewed and edited the content and take full responsibility for the published work.

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