Structural and Magnetic Properties of Cr-Zn Nanoferrites Synthesized by Chemical Co-Precipitation Method

Rohit R. Powar****, Varsha D. Phadtare**, Vinayak G. Parale**, Sachin Pathak**, Pravina B. Piste***, and Dnyandevo N. Zambare[✉]*,†

*Department of Chemistry, Kisan Veer Mahavidyalaya, Wai 412803, Maharashtra, India

**Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Korea

***Department of Chemistry, Yashwantrao Chavan Institute of Science, Satara 415001, Maharashtra, India

(Received July 19, 2019; Revised August 12, 2019; Accepted August 13, 2019)

ABSTRACT

Chromium-doped zinc ferrite nanoparticles with the general formula $\text{Cr}_y\text{ZnFe}_{2-y}\text{O}_4$ ($y = 0, 0.025, 0.05, 0.075$, and 0.1) were synthesized by a surfactant-assisted chemical co-precipitation route using metal nitrate salt precursors. The phase purity and structural parameters were determined by powder X-ray diffraction. The concentration of Cr^{3+} doped into ZnFe_2O_4 (ZF) noticeably affected the crystallite size, which was in the range of 22 nm to 36 nm, and all samples showed a single cubic spinel structure without any secondary phase or impurities. The lattice parameter, X-ray density, and skeletal density increased with an increase in the Cr-doping concentration; on the other hand, a decreasing trend was observed for the particle size and porosity. The influence of Cr^{3+} substitution on ZF magnetic properties were studied under an applied field of 15 kOe. The overall results revealed that the incorporation of a small amount of Cr dopant changed the structural, electrical, and magnetic properties of ZF.

Key words : Cr-Zn ferrites, Spinel oxides, Chemical co-precipitation, Thermal stability, Magnetic properties

1. Introduction

Recently, tertiary mixed metal oxide nanoparticles with cubic spinel structures have been identified as the most promising materials for electrochemical energy storage applications, televisions, transformers, magnetic recording media, biomedical applications, etc., because of their exceptional physicochemical, mechanical, magnetic, and dielectric properties.^{1–6)} Extensive efforts have been devoted to developing a modest, stable, and effective synthesis process for nanosized materials, which can control their structural parameters and impart a high specific surface area.^{7,8)} In recent decades, size-tunable ferrite particles with a cubic spinel structure have been identified as remarkable materials because of their exceptional physicochemical properties. The cubic spinel ferrite has received significant research importance because of their outstanding, versatile, and multifield applications. Among cubic spinel ferrite materials, zinc ferrites are unique and technologically important, and find a variety of applications in water splitting, biomedicine, photocatalysts, transformer cores, microwave technology, magnetic recording media, and gas sensors.^{9–13)} The general formula of the cubic spinel structure is AB_2O_4 , where “A” is a bivalent metal ion and “B” is a trivalent

metal ion. The spinel ferrite crystal structure consists of a cubic closed arrangement of oxygen ions with 8 tetrahedral (A-site) and 16 octahedral (B-site) interstitial sites in the unit cell.¹⁴⁾ Therefore, in spinel ferrites, an enormous amount of vacant A and B positions are available for cations to migrate, amongst the interstitial sites. Nanocrystalline n-type semiconductor ZnFe_2O_4 has a typical spinel structure with Zn^{2+} ions at the tetrahedral interstitial sites and Fe^{3+} ions distributed between the tetrahedral and octahedral interstitial sites.¹⁵⁾ The physicochemical, electrical, and magnetic properties of spinel ferrites are noticeably affected by the addition of cations and their preferential distribution among the tetrahedral and octahedral interstitial sites, as well as particle size reduction (i.e., to produce a nanosized material) via manipulation of the preparation method to a great extent. These properties are dependent on the synthesis method, calcination temperature, compound composition, and type and concentration of the dopants.^{16,17)}

Notably, the spinel ferrites nickel ferrite (NiFe_2O_4) and zinc ferrite (ZnFe_2O_4) have received extensive research interest because of their excellent chemical stability, excellent catalytic and optical properties, low cost, and facile industrial-scale preparation, and they are favorably used in the microwave industry. ZnFe_2O_4 is a soft magnetic material with unusual physical, chemical, electrical, and magnetic properties, and these properties are mostly dependent on the Fe^{2+} to Fe^{3+} transformation. In addition, the interchange of trivalent metal ions in zinc ferrite considerably affects the physicochemical, magnetic, and electrical proper-

†Corresponding author : Dnyandevo N. Zambare

E-mail : dnzambare1966@gmail.com

Tel : +91-2167-220130 Fax : +91-2167-220130

ORCID

<https://orcid.org/0000-0002-4294-7986>

ties. Chromium zinc ferrites are extensively studied soft magnetic materials and they can be easily obtained via the introduction of Cr^{3+} ions into the unit cell of zinc ferrite because their size is analogous to that of Fe^{3+} ions.^{9,18-21} Currently, nanoparticles of spinel ferrite are synthesized by different techniques such as chemical co-precipitation,^{22,23} microwave combustion,^{24,25} hydrothermal,²⁶ sol-gel,²⁷ and ceramic²⁸ methods.

In the present work, nanoparticles of Cr^{3+} -doped ZnFe_2O_4 with the general formula $\text{Cr}_y\text{ZnFe}_{2-y}\text{O}_4$ (CrZF), where $y = 0.0, 0.025, 0.05, 0.075$, and 0.1 , were prepared by the chemical co-precipitation technique in the presence of a surfactant. This technique is a productive, cheap, and simple surfactant-assisted chemical process that can yield a large quantity of smaller particles with the preferred structure, hierarchy, and desired elemental composition at a lower sintering temperature, compared to the traditional ceramic technique. The effect of Cr doping (low dopant concentration) on the physicochemical properties of undoped zinc ferrite (ZF) is reported here.

2. Experimental Procedure

2.1. Synthesis and characterization

Nanosized particles of spinel ferrite CrZF ($y = 0.0, 0.025, 0.05, 0.075$ and 0.1) were produced by a surfactant-assisted chemical co-precipitation method. The nitrate salts of metal precursors (analytical reagent) were purchased from Thomas Baker (Chemicals) Pvt. Ltd., Mumbai, India. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), n-hexadecyltrimethylammonium bromide (CTAB), 30% aqueous ammonia (NH_3), and lab-made double distilled water were used for the synthesis. All chemicals were used as received without further refinement.

The detailed synthesis procedure of the nanoferrites has been reported in our previous publication.²² To remove organics, the co-precipitated mixture was preheated up to 350°C in a muffle furnace for 2 h. The furnace was allowed to cool down, and then, the powder was removed and milled with acetone to obtain a homogeneous mixture using pestle and mortar. The air-dried samples were heated at 750°C for 4 h in air, as depicted in Fig. 1. Finally, a soft nanocrystalline CrZF powder was obtained by milling with a pestle and mortar. The endothermic and exothermic behaviors and thermal stability of the spinel ferrites were studied by thermogravimetry-differential thermal analysis (TG-DTA, Nietzsche STA 409 TG DSE) in the temperature range from

Fig. 1. Flow chart for Cr-doped zinc ferrite formation.

30°C to 1000°C in synthetic air at a heating rate of 10°C·min⁻¹. The phase purity and structural parameters of ferrites were determined by X-ray diffraction (XRD, PW-1710 Philips) with the Cu K α radiation ($\lambda = 1.5405$ Å) in scanning range of 10–80°. Fourier-transform infrared (FT-IR) spectroscopy (Perkin Elmer Spectrum One spectrophotometer equipped with an attenuated total reflectance (ATR) accessory) was performed using KBr pellets in the wavenumber range of 350–800 cm⁻¹. The topographical microstructures of the thick film samples were determined by field-emission scanning electron microscopy (FE-SEM) using a SIGMA HV model (in the magnification range from 50x to 100,000x) equipped with an energy-dispersive X-ray (EDS) spectroscopy analyzer (for chemical composition and phase purity determination). The prepared ferrite particle dimensions were determined by a particle size analyzer. The specific surface area and pore size values were calculated using the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) techniques by N₂ adsorption-desorption measurements (Quantachrome Instruments v10.0). DC electrical resistivity measurements were carried out using a digital picoammeter (DPM-111) to record the current at a constant voltage across the sample by the two-probe method. Room-temperature magnetic measurements up to a maximum field of 15 kOe were carried out using a vibrating sample magnetometer (VSM, PAR EG&G 4500).

3. Results and Discussion

3.1. TG-DTA analysis

The characteristic TG-DTA curve for the chemically coprecipitated CrZF sample ($y = 0.05$) is displayed in Fig. 2, from which the thermal stability and phase transition temperature of the ferrites were determined. The TG curve of the ZnCr_{0.05}Fe_{1.95}O₄ ferrite revealed that the total weight loss was ~31.5%. In addition, the TG curve exhibited minor (~9%) and major (~22.5%) weight loss steps in the tem-

Fig. 2. TG-DTA curves of the as-prepared Cr_yZnFe_{2-y}O₄ ($y = 0.05$) sample.

perature range of 25–135°C and 190–320°C, respectively. The minor weight loss was attributed to the loss of moisture and major weight loss was attributed to the decomposition of the carbon-based matrix and conversion of hydroxides into oxides.²⁹ No further weight loss was observed between 414°C and 1000°C. The DTA curve showed a major exothermic peak at 248°C, suggesting the occurrence of combustion of the organic matrix and conversion of the precipitate into metal oxide, which was correlated with the major weight loss step in the TG curve. The plateau observed between 415°C and 1000°C in the TG curve indicated the formation of crystalline ZnCr_{0.05}Fe_{1.95}O₄ ferrite without any further weight loss. Thus, a single cubic spinel ferrite phase was formed due to the conversion of the valence state of the metal oxides at high sintering temperatures.

3.2. XRD analysis

Figure 3 presents the XRD patterns of CrZF ($y = 0.0$, 0.025, 0.05, 0.075, and 0.1) samples annealed at 750°C for 4 h. All XRD patterns were matched with those of ZnFe₂O₄ (JCPDS card numbers 84-0314 and 89-1012). The major diffraction peaks were assigned to the (111), (220), (311), (222), (400), (422), (511), (440), and (531) planes, and the most intense diffraction peak was assigned to the (311) plane, evidently confirming the formation of a cubic spinel structure. The lattice constant (a) was calculated using equation (1).

$$a = d(h^2 + k^2 + l^2)^{1/2} \quad (1)$$

where h , k , and l are Miller indices of the crystal planes and d is the interplanar distance for the hkl planes. The value of “ a ” marginally decreased with an increase in the Cr concentration due to the different sizes of Cr³⁺ (0.615 Å) and Fe³⁺ (0.645 Å). Table 1 demonstrates the influence of Cr concentration on the lattice constants of CrZF samples; the results

Fig. 3. XRD patterns of Cr_yZnFe_{2-y}O₄ ($y = 0, 0.025, 0.050, 0.075, \text{ and } 0.1$) samples sintered at 750°C for 4 h.

Table 1. The Influence of Cr³⁺ Doping (y) on the Structural Parameters of Samples Cr_yZnFe_{2-y}O₄ where (0 ≤ y ≤ 0.1)

Composition (y)	Crystal-lite size 'D _{XRD} ' (nm)	Lattice constant 'a' (Å)	Unit cell volume (Å ³)	X-ray density (g/cm ³)	Physical density (g/cm ³)	Bond length		Ionic radii	
						A-O	B-O	r _A	r _B
0.0	22.39	8.407	594.19	5.351	4.553	1.9183	2.0389	0.5983	0.7189
0.025	23.90	8.458	605.06	5.255	4.381	1.9269	2.0480	0.6069	0.728
0.05	30.29	8.425	598.01	5.316	4.354	1.9424	2.0405	0.6224	0.7205
0.075	27.27	8.477	609.15	5.205	4.361	1.9429	2.0410	0.6229	0.721
0.1	36.13	8.472	608.08	5.229	4.394	1.9428	2.0408	0.6227	0.719

were consistent with Vegard's law.^{21,30)}

The average crystallite size (D_{XRD}) values for the powder samples were determined using the Debye-Scherrer formula:

$$D_{XRD} = \frac{0.89\lambda}{\beta \cos \theta} \quad (2)$$

Where, λ stands for the incident X-ray wavelength (Cu Kα radiation), β stands for full-width at half maximum (FWHM) in radians in the 2θ scale, θ is the Bragg angle, D_{XRD} is the crystallite size in nm. To obtain β and θ values for all samples, the Gaussian fitting model was adopted. The particle sizes of the samples increased due to the replacement of Fe³⁺ cations by Cr³⁺ ions with a smaller radius. D_{XRD} increased from 22.39 nm to 36.13 nm with an increase in the Cr concentration (y = 0.0–0.1). The X-ray densities (dx) of all CrZF samples were determined using the following formula³¹⁾:

$$dx = \frac{ZM}{Na^3} \quad (3)$$

where Z = a constant (Z = 8; the total number of molecules in each unit cell), M = molecular weight (g·mole⁻¹), and N = Avogadro's number (6.023 × 10²³ atoms·mole⁻¹).

The skeletal density (ds) values were obtained by measuring the dry and suspended weights of the samples in xylene according to Archimedes' principle:

$$ds = \frac{w\rho}{w-w'} \quad (4)$$

where w is the weight of the sample in air (g), w' is the weight of the sample in xylene (g), and ρ is the density of xylene (g·cm⁻³).

From the skeletal and X-ray densities of the samples, the percentage porosity (p) was determined using the following relation³²⁾:

$$p = \left(1 - \frac{ds}{dx}\right) 100\% \quad (5)$$

The tetrahedral and octahedral site bond lengths (A-O, B-O) and ionic radii (r_A, r_B) of the cubic spinel structures were calculated using the following formulae³³⁾.

$$A-O = \left(u - \frac{1}{4}\right)a\sqrt{3} \quad (6)$$

$$B-O = \left(\frac{5}{8} - u\right)a \quad (7)$$

$$r_A = \left(u - \frac{1}{4}\right)a\sqrt{3} - r(O^{2-}) \quad (8)$$

$$r_B = \left(\frac{5}{8} - u\right)a - r(O^{2-}) \quad (9)$$

where, u and r(O²⁻) are the oxygen ion parameter and radius of oxygen ion (~ 1.32 Å), respectively. Table 1 clearly demonstrates the effect of Cr doping concentration on the crystallite size, lattice constant, X-ray density, physical density, bond length, ionic radii, etc.

3.3. FT-IR analysis

FT-IR spectroscopy was performed to determine the fundamental changes and tetrahedral and octahedral sites of spinel ferrites. Moreover, from the FTIR spectra, the impurity states and chemical substances present on the particle surface were determined. Fig. 4 shows the transmittance spectra with two main broad metal-oxygen bands in the range of 400–600 cm⁻¹, indicating the presence of a pure cubic CrZF spinel phase in all samples.³⁴⁾ The higher wave number u₁ absorption band, which is generally observed in the range of 544–569 cm⁻¹, was attributed to the vibration of

Fig. 4. FTIR spectra of Cr_yZnFe_{2-y}O₄ (y = 0, 0.025, 0.050, 0.075, and 0.1) samples sintered at 750°C.

Table 2. The Effect of Cr^{3+} Doping (y) on Porosity, Grain Size, and Position of FTIR Absorption Bands (ν_1 , ν_2) of Sample $\text{Cr}_y\text{ZnFe}_{2-y}\text{O}_4$ where ($0 \leq y \leq 0.1$)

Chromium concentration (y)	Porosity (%)	Grain size G_d (μm)	Absorption band (cm^{-1})		$\nu_1 - \nu_2$
			ν_1	ν_2	
0.0	17.52	0.23	569	439	130
0.025	19.95	0.22	550	435	115
0.05	22.09	—	551	432	119
0.075	19.35	0.20	549	432	117
0.1	19	0.19	544	436	108

the tetrahedral metal-oxygen and the lower wave number ν_2 absorption band observed in the range of $432\text{--}439\text{ cm}^{-1}$ was attributed to octahedral metal-oxygen bond stretching vibration. The absorption bands at 439 cm^{-1} and 569 cm^{-1} were assigned to the octahedral and tetrahedral sites of spinel zinc ferrite. The ν_1 band observed at around $544\text{--}551\text{ cm}^{-1}$ for the Cr-doped spinel CrZF ($y = 0.025, 0.05, 0.075$, and 0.1) was assigned to the tetrahedral site and the ν_2 band observed at $432\text{--}436\text{ cm}^{-1}$ was assigned to the $\text{Fe}^{3+}\text{--O}^{2-}$ vibration at the octahedral location; moreover, the shift in the ν_1 band location was attributed to the increase in the doping amount of Cr^{3+} ions in zinc ferrite. As the Cr concen-

Fig. 5. FE-SEM and EDS data for $\text{Cr}_y\text{ZnFe}_{2-y}\text{O}_4$ ($y = 0, 0.025, 0.050, 0.075$, and 0.1) samples sintered at 750°C .

tration increased, ν_1 decreased (i.e., from 550 cm^{-1} for $\text{Cr}_{0.025}\text{ZnFe}_{1.975}\text{O}_4$ to 544 cm^{-1} for $\text{Cr}_{0.1}\text{ZnFe}_{1.9}\text{O}_4$). This indicated that the Cr^{3+} ions replaced a proportional amount of Fe^{3+} ions in the octahedral sites, resulting in a reduction in the length of the metal-oxygen bond, which was reflected by an increase in the broadening of the absorption band, as presented in Table 2.²¹⁾

3.4. Morphological and elemental analysis

The FE-SEM images of CrZF ($y = 0.0, 0.025, 0.075$, and 0.1) samples sintered at 750°C are presented in Fig. 5 (a-d). In Fig. 5, nearly uniform and agglomerated grains are observed. The grain size of the sample is usually calculated by the linear intercept method using equation (10).³⁵⁾

$$G_d = \frac{1.5 L}{MN} \quad (10)$$

where L , M , and N are the total length of the test line, magnification, and number of intercepts, respectively. The morphology and size of particles were influenced by the Cr-doping content and calcination temperature, and the size ranged from 0.19–0.23 μm . With an increase in the Cr content, the particle size decreased from 0.23 μm to 0.19 μm , which was larger than D_{XRD} of CrZF thick films.

The percentage elemental composition of the prepared CrZF thick film was investigated by the EDS technique. Fig. 5(e-h) present the EDS profiles of the CrZF samples. EDS was performed to verify homogeneity of the prepared samples and examine the presence of impurities originating from the synthesis process. The compositional percentages of Fe, Zn, Cr, and O in the Cr-doped zinc ferrite samples are listed in Table 3 as a function of the Cr doping concentration. The EDS data for the CrZF ($y = 0.0, 0.025, 0.075$, and 0.1) samples revealed the doping level (wt.%) of Cr in the samples to be 0.69, 1.25, and 1.51 for $y = 0.025, 0.075$, and 0.1 , respectively. However, the wt.% of Fe decreased in the order 50.95, 43.57, 46.60, and 45.07 with increasing y (0.0, 0.025, 0.075, and 0.1, respectively).

3.4. BET analysis

N_2 adsorption-desorption measurements were performed to determine the changes in the specific surface area and pore size as a function of the Cr substitution level. Type (IV) hysteresis loops for all CrZF ($y = 0.0$ -0.1) samples obtained at 77 K are depicted in Fig. 6; the Type (IV) hysteresis loop

Fig. 6. N_2 adsorption-desorption isotherms of $\text{Cr}_y\text{ZnFe}_{2-y}\text{O}_4$ ($y = 0, 0.025, 0.050, 0.075$, and 0.1) samples.

is characteristic to porous materials.³⁶⁾ The surface area values for nanocrystalline CrZF ($y = 0.0, 0.025, 0.05, 0.075$ and 0.1) samples annealed at 750°C as a function of the Cr doping level are tabulated in Table 3. The specific surface area values for CrZF ($y = 0.0, 0.025, 0.05, 0.075$, and 0.1) samples are 5.245, 10.411, 5.265, 4.422, and 11.689 $\text{m}^2\cdot\text{g}^{-1}$, and the cumulative pore volumes are found to be 0.025, 0.033, 0.021, 0.020, and 0.039 $\text{cm}^3\cdot\text{g}^{-1}$, respectively. The BJH pore volume analysis revealed an average pore diameter of ~ 3 –4 nm.

3.5. DC electrical resistivity analysis

Spinel ferrites are well-known high-resistance materials and their conductivity is determined by the drift mobility of electric carriers between ferrous and ferric ions (with +2 and +3 valence states), which are thermally activated. The temperature-dependent electrical resistivity (ρ) of CrZF samples was investigated in the temperature range of 30–600 $^\circ\text{C}$. Fig. 7 presents the plot of temperature dependency of the DC electrical resistivity versus $10^3/T$. The electrical resistivity of the synthesized samples exhibited temperature-dependent brakes among linear shape with increasing temperature, suggesting their semi-conductive nature. This change in the resistivity with the Cr content could be explained on the basis of the hopping mechanism. It is well

Table 3. The Variations in Physical Properties of Samples $\text{Cr}_y\text{ZnFe}_{2-y}\text{O}_4$ where ($0 \leq y \leq 0.1$) Due Cr^{3+} Concentration

Chromium concentration (y)	Pore size (nm)	Surface area (m^2/g)	Pore volume (cm^3/g)	Wt. Abundance (%)			
				Iron	Oxygen	Zinc	Chromium
0.0	3.822	5.245	0.025	50.95	34.86	14.55	–
0.025	3.408	10.411	0.033	43.57	29.47	13.02	0.69
0.05	3.054	5.265	0.021	–	–	–	–
0.075	3.819	4.422	0.020	46.60	29.51	10.98	1.25
0.1	3.820	11.689	0.039	45.07	30.95	10.56	1.51

Fig. 7. Temperature-dependence of DC electrical resistivity against $1000/T$ for $\text{Cr}_y\text{ZnFe}_{2-y}\text{O}_4$ ($y = 0, 0.025, 0.050, 0.075$, and 0.1) samples.

known that the distribution of cations, grain size, and porosity have a strong influence on the resistivity of ferrites. At high temperatures, ferrites acquire thermal energy and oxygen ions escape from CrZF in the form of ZnO, creating oxygen vacancies to maintain charge balance transformation of the Fe^{3+} to Fe^{2+} ions, retaining spinel lattice neutrality. In undoped ZF, Zn^{2+} and Fe^{3+} ions occupy the tetrahedral (A) and octahedral (B) interstitial sites, respectively, whereas in Cr-doped zinc ferrite, with increasing Cr^{3+} doping amount, the concentration of Fe^{3+} ions at the B-sites decreases; consequently, Cr^{3+} ions at the B-sites hamper electron hopping between Fe ions by blocking the $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ exchange, which increases the resistivity. Notably, the amount of Fe^{3+} ions at the octahedral sites decreases as the Cr^{3+} doping concentration increases and Cr^{3+} ions do not take part in the hopping mechanism. As observed in Fig. 7, the resistivity increased as the Cr^{3+} substitution level in Cr-doped zinc ferrite increased. The mesoporous CrZF nanostructures were composed of grains with sizes in the range of $0.19\text{--}0.23\text{ }\mu\text{m}$. The samples contained numerous grain boundaries, which acted as obstacles to the flow of electrons, obstructing hopping of charge carriers; this resulted in increased resistivity.³⁷⁾

3.6. Magnetic analysis

The room-temperature magnetization vs. applied field curves (M-H loops) for Cr-Zn ferrite samples are shown in Fig. 8. For all samples, the magnetization reached saturation at a magnetic field of 15000 Oe . The magnetic properties were determined from Fig. 8 and all values are listed in Table 4. The saturation magnetization (M_s) significantly increased with the addition of Cr^{3+} . For CrZF samples, when y was increased from 0.025 to 0.1 , the M_s value increased from $0.0237\text{ emu}\cdot\text{g}^{-1}$ to $0.1498\text{ emu}\cdot\text{g}^{-1}$. Mostly, the Cr^{3+} replaced the Fe^{3+} in octahedral sites, decreasing the magnetic moment of CrZF at low doping concentrations. H_c values were clearly affected by Cr substitution. As observed from Table 4, with an increase in the Cr^{3+} concentration, the

Fig. 8. Magnetic hysteresis loops of $\text{Cr}_y\text{ZnFe}_{2-y}\text{O}_4$ ($y = 0.025, 0.05, 0.075$, and 0.1) samples at room temperature.

H_c value decreased for samples with $y = 0.025$ and 0.05 , while it increased for samples with $y = 0.075$ and 0.1 . As reported, the Co-doped ZnFe_2O_4 sample exhibited the highest coercivity value ($\sim 1834\text{ Oe}$), which was attributed to the particle size effect, nature of the dopant, and high doping concentration.²²⁾

As the applied field increased, the magnetization increased from zero in both directions, and saturation in the hysteresis loop was not observed, which could be due to the presence of non-magnetic Zn^{2+} ions and weakly magnetic Cr^{3+} ions in the spinel ferrites. Usually, three kinds of superexchange interactions occur in spinel ferrites (A-A, B-B, and A-B), according to Neel's two-sublattice model. The strength of A-B interaction was higher than those of the other two interactions. ZnFe_2O_4 showed the lowest magnetization.²²⁾ However, doping of Cr into zinc ferrite slightly decreased the magnetization for samples with $y = 0.025$ and 0.05 due to the substitution of weakly magnetic Cr^{3+} ions from B-site replaces the comparatively high magnetic Fe^{3+} ions in B-site was affected due to the A-B interaction. Non-linear magnetization values were obtained because of the presence of Zn^{2+} ions, which caused spin canting. The $\text{Cr}_{0.025}\text{ZnFe}_{1.975}\text{O}_4$ sample exhibited a low coercivity value of 40 Oe because the replacement of Fe^{3+} by Cr^{3+} ions reinforced the sublattice interaction, indicating that the particle was easily magne-

Table 4. The Effects of Cr^{3+} Doping Concentration on the Magnetic Properties of Samples $\text{Cr}_y\text{ZnFe}_{2-y}\text{O}_4$ where ($0.025 \leq y \leq 0.1$)

Composition 'y'	M_s (emu/cc)	M_r (emu/cc)	M_r/M_s	H_c (Oe)
0.025	0.0237	0.0022	0.0912	40
0.050	0.0442	0.0042	0.0943	50
0.075	0.0472	0.0019	0.0412	164
0.1	0.1498	0.0166	0.1109	70

tized without any flux loss. The changing nature of hysteresis loops with increasing Cr concentration makes this type of ferrites suitable for various applications, such as microwave devices, transformer cores, etc.

4. Conclusions

In the present study, we produced compositionally different nanoparticles of CrZF ($0 \leq y \leq 0.1$) by combining highly soluble nitrate salts of Fe, Cr, and Zn in the presence of CTAB by a chemical co-precipitation technique at a lower calcination temperature compared to that used in the ceramic method. The TG analysis result of the as-prepared sample revealed that above 450°C, the stable phase of chromium zinc ferrite was formed. The XRD results proved that the crystallite size increased from ~ 22 nm to 36 nm with the substitution of Cr³⁺ into the single cubic spinel structure for all CrZF samples. Furthermore, Cr³⁺ doping-induced changes were investigated by FTIR spectroscopy on the basis of the bond stretching vibrations of tetrahedral and octahedral metal complexes in the range of 400–600 cm⁻¹. After doping of Cr³⁺ into zinc ferrite samples, certain deviations in the skeletal and X-ray densities, crystallite size, unit cell volume, and ionic length of the tetrahedral and octahedral sites were observed for ZnFe₂O₄. The FE-SEM images revealed that all samples were porous and the particles were nearly uniform shaped with an average size of 0.19–0.23 μm; the average size decreased after the incorporation of Cr³⁺ due to agglomeration at the elevated calcination temperature. The influence of Cr³⁺ ions caused noticeable variations in the structural, morphological, electrical, and magnetic properties of the CrZF ($0 \leq y \leq 0.1$) spinel ferrite, which strongly depended on the chemical composition, size, and preferential distribution of cations at (A) and (B) sites. Thus, Cr doping in the zinc ferrite increased the resistivity. The incorporation of Cr³⁺ ions into zinc ferrite led to a decrease in the saturation magnetization, coercivity, and magnetic moment at very low concentrations, and an increase in the magnetic moments of the unit cells at high concentrations. It was confirmed that the Cr-Zn ferrites are soft magnetic materials, which could be used in transformers and motors.

Acknowledgments

The author (RRP) is grateful to the Department of Metallurgy, College of Engineering, Pune (COEP) Maharashtra, India for their help with the FE-SEM and EDS facility.

REFERENCES

1. Z. Wang, P. Hong, S. Peng, T. Zou, Y. Yang, X. Xing, Z. Wang, R. Zhao, Z. Yan, and Y. Wang, "Co(OH)₂@FeCo₂O₄ as Electrode Material for High Performance Faradaic Supercapacitor Application," *Electrochim. Acta*, **299** 312–19 (2019).
2. M. Amiri, M. Salavati-Niasari, and A. Akbari, "Magnetic Nanocarriers: Evolution of Spinel Ferrites for Medical Applications," *Adv. Colloid Interface Sci.*, **265** 29–44 (2019).
3. K. R. Sanadi, S. P. Patil, V. G. Parale, H. H. Park, G. S. Kamble, and H. M. Yadav, "Preparation of Cobalt Substituted Zinc Aluminum Chromite: Photocatalytic Properties and Suzuki Cross-Coupling Reaction," *J. Mater. Sci.: Mater. Electron.*, **29** [9] 7274–86 (2018).
4. V. D. Phadtare, V. G. Parale, G. K. Kulkarni, H. H. Park, and V. R. Puri, "Enhanced Microwave Absorption of Screen-Printed Multiwalled Carbon Nanotube/Ca_{1-x}Ba_xBi₂Nb₂O₉ ($0 \leq x \leq 1$) Multilayered Thick Film Composites," *J. Alloys Compd.*, **765** 878–87 (2018).
5. V. D. Phadtare, V. G. Parale, G. K. Kulkarni, H. H. Park, and V. R. Puri, "Microwave Dielectric Properties of Barium Substituted Screen Printed CaBi₂Nb₂O₉ Ceramic Thick Films," *Ceram. Int.*, **44** [7] 7515–23 (2018).
6. H. S. Jadhav, A. Roy, G. M. Thorat, and J. G. Seo, "Facile and Cost-Effective Growth of Highly Efficient MgCo₂O₄ Electro Catalyst for Methanol Oxidation," *Inorg. Chem. Front.*, **5** 1115–20 (2018).
7. V. G. Parale, K. Y. Lee, and H. H. Park, "Flexible and Transparent Silica Aerogel: An Overview," *J. Korean Ceram. Soc.*, **54** [3] 184–99 (2017).
8. A. I. Ivanets, V. Srivastava, M. Yu. Roshchina, M. Sillanpää, V. G. Prozorovich, and V. V. Pankov, "Magnesium Ferrite Nanoparticles as a Magnetic Sorbent for the Removal of Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺ from Aqueous Solution," *Ceram. Int.*, **44** [8] 9097–104 (2018).
9. D. S. Nair and M. Kurian, "Chromium-Zinc Ferrite Nanocomposites for the Catalytic Abatement of Toxic Environmental Pollutants under Ambient Conditions," *J. Hazardous Mater.*, **344** 925–41 (2018).
10. P. V. Gaikwad, R. J. Kamble, S. J. M. Gavade, S. R. Sabale, and P. D. Kamble, "Magneto-Structural Properties and Photocatalytic Performance of Sol-Gel Synthesized Cobalt Substituted Ni Cu Ferrites for Degradation of Methylene Blue under Sunlight," *Phys. B*, **554** 79–85 (2019).
11. R. A. Pawar, S. M. Patange, A. R. Shitre, S. K. Gore, S. S. Jadhav, and S. E. Shirsath, "Crystal Chemistry and Single-Phase Synthesis of Gd³⁺ Substituted Co–Zn Ferrite Nanoparticles for Enhanced Magnetic Properties," *RSC Adv.*, **8** [44] 25258–67 (2018).
12. M. M. Rahman, S. B. Khan, M. Faisal, A. M. Asiri, and K. A. Alamry, "Highly Sensitive Formaldehyde Chemical Sensor Based on Hydrothermally Prepared Spinel ZnFe₂O₄ Nanorods," *Sens. Actuators, B*, **171**–172 932–37 (2012).
13. J. Smit and H. P. J. Wijn, *Ferrites-Physical Properties of Ferromagnetic in Oxides Relation to Their Technical Application*; Wiley, New York, 1959.
14. H. Knock and H. Dannheim, "Temperature Dependence of the Cation Distribution in Magnesium Ferrite," *Phys. Status Solidi A*, **37** [2] K135–37 (1976).
15. S. S. Desai, S. M. Patange, A. D. Patil, S. K. Gore, and S. S. Jadhav, "Effects of Zn²⁺-Zr⁴⁺ Ions on the Structural, Mechanical, Electrical, and Optical Properties of Cobalt Ferrites Synthesized via the Sol–Gel Route," *J. Phys. Chem. Solids*, **133** 171–77 (2019).

16. N. Rezlescu, E. Rezlescu, P. D. Popa, M. L. Craus, and L. Rezlescu, "Copper Ions Influence on the Physical Properties of a Magnesium-Zinc Ferrite," *J. Magn. Magn. Mater.*, **182** [1–2] 2670–79 (2017).
17. M. Wang, M. Yang, X. Zhao, L. Ma, X. Shen, and G. Cao, "Spinel $\text{LiMn}_{2-x}\text{Si}_x\text{O}_4$ ($x < 1$) through Si^{4+} Substitution as a Potential Cathode Material for Lithium-Ion Batteries," *Sci. China Mater.*, **59** [7] 558–66 (2016).
18. M. Lakshmi, K. V. Kumar, and K. Thyagarajan, "An Investigation of Structural and Magnetic Properties of Cr–Zn Ferrite Nanoparticles Prepared by a Sol–Gel Process," *J. Nanostruct. Chem.*, **5** [4] 365–73 (2015).
19. D. S. Nair and M. Kuriand, "Chromium-Zinc Ferrite Nanocomposites for the Catalytic Abatement of Toxic Environmental Pollutants under Ambient Conditions," *J. Hazard. Mater.*, **344** 925–41 (2018).
20. A. I. Borhan, V. Hulea, A. R. Iordan, and M. N. Palamaru, " Cr^{3+} and Al^{3+} Co-Substituted Zinc Ferrite: Structural Analysis, Magnetic and Electrical Properties," *Polyhedron*, **70** 110–18 (2014).
21. D. S. Nair and M. Kurian, "Chromium-Zinc Ferrite Nanocomposites for the Catalytic Abatement of Toxic Environmental Pollutants under Ambient Conditions," *J. Hazard. Mater.*, **344** 925–41 (2018).
22. R. R. Powar, V. D. Phadtare, V. G. Parale, H.-H. Park, S. Pathak, P. R. Kamble, P. B. Piste, and D. N. Zambare, "Structural, Morphological, and Magnetic Properties of $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$) Prepared Using a Chemical Coprecipitation Method," *Ceram. Int.*, **44** [17] 20782–89 (2018).
23. M. Ebrahim, R. R. Shahraki, S. A. S. Ebrahimi, and S. M. Masoudpanah, "Magnetic Properties of Zinc Ferrite Nanoparticles Synthesized by Coprecipitation Method," *J. Supercond. Novel Magn.*, **27** [6] 1587–92 (2014).
24. A. Manikandan, J. J. Vijaya, M. Sundararajan, C. Meganathan, L. J. Kennedy, and M. Bououdina, "Optical and Magnetic Properties of Mg-doped ZnFe_2O_4 Nanoparticles Prepared by Rapid Microwave Combustion Method," *Superlattices Microstruct.*, **64** 118–31 (2013).
25. N. Kasapoglu, A. Baykal, Y. Koseoglu, and M. S. Toprak, "Microwave-Assisted Combustion Synthesis of CoFe_2O_4 with Urea, and its Magnetic Characterization," *Scr. Mater.*, **57** [5] 441–44 (2007).
26. Y. Koseoglu, M. I. O. Oleiwi, R. Yilgin, and A. N. Kocbay, "Effect of Chromium Addition on the Structural, Morphological and Magnetic Properties of Nano-Crystalline Cobalt Ferrite System," *Ceram. Int.*, **38** [8] 6671–76 (2012).
27. A. A. Birajdar, S. E. Shirsath, R. H. Kadam, S. M. Patange, D. R. Mane, and A. R. Shitre, "Frequency and Temperature Dependent Electrical Properties of $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Cr}_x\text{Fe}_{2-x}\text{O}_4$ ($0 \leq x \leq 0.5$)," *Ceram. Int.*, **38** [4] 2963–70 (2012).
28. K. A. M. Khalaf, A. D. Al-Rawas, H. M. Widadallah, K. S. Al-Rashdi, A. Sellai, A. M. Gismelseed, M. Hashim, S. K. Jameel, M. S. Al-Ruqeishi, K. O. Al-Riyami, M. Shongwe, and A. H. Al-Rajhi, "Influence of Zn^{2+} Ions on the Structural and Electrical Properties of $\text{Mg}_{1-x}\text{Zn}_x\text{FeCrO}_4$ Spinel," *J. Alloys Compd.*, **657** 733–47 (2016).
29. V. D. Phadtare and V. R. Puri, "Studies on Electrical and Dielectric Properties of Co-Precipitated Aurivillius Phase $\text{Ca}_{1-x}\text{Ba}_x\text{Bi}_2\text{Nb}_2\text{O}_9$ Ceramics," *Ceram. Int.*, **42** [7] 8581–86 (2016).
30. A. R. Denton and N. W. Ashcroft, "Vegard's Law," *Phys. Rev. A*, **43** 3161 (1991).
31. B. D. Culity, Elements of X-ray Diffraction; Vol. 99, p. 96, Addison Wesley Pub Co Inc, 1967.
32. U. R. Ghodake, N. D. Chaudhari, R. C. Kambale, J. Y. Patil, and S. S. Suryavanshi, "Effect of Mn^{2+} Substitution on Structural, Magnetic, Electric and Dielectric Properties of Mg-Zn Ferrites," *J. Magn. Magn. Mater.*, **407** 60–8 (2016).
33. K. J. Standley, Oxide Magnetic Materials, Oxford at Clarendon Press, London, 1962.
34. R. D. Waldron, "Infrared Spectra of Ferrites," *Phys. Rev.*, **99** [6] 1727 (1955).
35. M. I. Mendelson, "Average Grain Size in Polycrystalline Ceramic," *J. Am. Ceramic. Soc.*, **52** [8] 443–46 (1969).
36. V. Jeseentharani, M. George, B. Jeyaraj, A. Dayalan, and K. S. Nagaraja, "Synthesis of Metal Ferrite (MFe_2O_4 , $\text{M}=\text{Co}, \text{Cu}, \text{Mg}, \text{Ni}, \text{Zn}$) Nanoparticles as Humidity Sensor Materials," *J. Exp. Nanosci.*, **8** [3] 358–70 (2013).
37. R. H. Kadam, A. Karim, A. B. Kadam, A. S. Gaikwad, and S. E. Shirsath, "Influence of Cr^{3+} Substitution on the Electrical and Magnetic Properties of $\text{Ni}_{0.4}\text{Cu}_{0.4}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ Nanoparticles," *Int. Nano Lett.*, **2** 28 (2012).