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Influence of Zn-Zr substitution on the crystal chemistry and magnetic properties of CoFe₂O₄ nanoparticles synthesized by sol-gel method

S.S. Desai^a, Sagar E. Shirsath^{b,*}, Khalid Mujasam Batoo^{c,**}, Syed Farooq Adil^d, Mujeeb Khan^d, S.M. Patange^{a,***}

^a Department of Physics, Shrikrishna Mahavidyalaya, Gunjoti, MS, India

^b School of Material Science and Engineering, The University of New South Wales, Kensington, New South Wales, 2052, Australia

^c King Abdullah Institute for Nanotechnology, King Saud University, P.O. Box 2455, Riyadh, 11451, Saudi Arabia

^d Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh, 11451, Saudi Arabia

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ABSTRACT

The Zn-Zr co-substituted cobalt ferrite nanoparticles (CoZn_xZr_xFe_{2-2x}O₄, x = 0.0-0.4) were synthesized by sol gel auto combustion route. The formation of cubic phase of Co ferrite was revealed from the X-ray diffractograms of the powder samples. The additional α -Fe₂O₃ and ZrO₂ phases were occurred for \geq 20% Zn-Zr substitution. The lattice parameters obtained by extrapolating Nelson-Riley function shows increase in its values with the Zn-Zr substitution. The particle size shows increasing trend with the Zn-Zr substitution. The cation distribution obtained from the Rietveld refinement of XRD estimate the equal preference of Zn ons preferred tetrahedral A site whereas most of the Zr ions occupy octahedral B site. The decrease in Fe ions with the Zn-Zr substitution resulted in the decrease in coercivity and saturation magnetization of the ferrites. Zero field cooled and field cooled magnetization plots of the ferrites reveals the ferromagnetic behaviour of the prepared ferrite samples. The blocking temperature does not vary significantly with the varying Zn-Zr substitution. The Mössbauer study confirms the weakening of the magnetic Fe ions. The decrease in coercivity with moderate saturation magnetization could make this material suitable for electronic devices.

1. Introduction

Nowadays, the nanostructured materials are widely used for frontier research areas because of their good physicochemical characteristics which are not shown by many material of similar compositions in their bulk counterpart [1]. Amon the many nanomaterials, transition type metal oxide based materials are gaining more attention by researchers due to a wide range of broad spectrum of applications such as medical, energy storage, fabrication of advanced devices, etc. [2–5]. The ferrites are having a unique characteristic of high surface to volume ratio leading them to use it phenomena of nanomagnetism [6]. The various single dopant and mixed valent dopants are added to improve magnetic properties of ferrites. Recently many researchers have well developed various methods of ferrite preparation such as ceramic, high energy ball

milling and flash combustion methods to improve the properties [1,7].

CoFe₂O₄ (CFO) is an inverse spinel ferrite (space group *Fd3m*; no. 227) possessing cubic crystal system. CoFe₂O₄ shows a moderate saturation magnetization (Ms) (80 emu/g), and has a positive first-order magnetocrystalline anisotropy constant ($K_I \sim 2 \times 10^6$ erg/cm³) resulting in a high coercivity (*Hc*) [8,9]. These properties making CoFe₂O₄ a promising material for many applications including; magnetic spin filters [10], spintronics devices [11], recording media [12], photocatalysis [13,14], ceramic pigments [15]. All these applicabilities are mainly depends on the characteristic values of Ms and *Hc* and thus researchers are focusing to improve these parameters either by synthesizing CoFe₂O₄ with different techniques or by substituting various transition metal ions in CoFe₂O₄.

Morphology of particles along with their size and distribution are the

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PRINCIPAL Dr Vithalrao Vikhe Patil College of Engineering Ahmednagar

^{*} Corresponding author

^{**} Corresponding author.

^{***} Corresponding author.

E-mail addresses: shirsathsagar@hotmail.com (S.E. Shirsath), kbatoo@ksu.edu.sa, khalid.mujasam@gmail.com (K. Mujasam Batoo), smpatange@rediffmail.com (S.M. Patange).

Physica B: Physics of Condensed Matter 596 (2020) 412400

major factors to manipulate the structural, electrical and magnetic properties of ferrites [16]. Apart from these factors the properties of spinel ferrites are strongly depend on the substitution of tetravalent (+4), trivalent (+3) and divalent (+2) ions and their site occupancies among the available octahedral B- and tetrahedral A-sites. Further, the combination of tetravalent and divalent ions $Co^{2+}-Zn^{2+}-Zr^{4+}$ [17], $Cu^{2+}-Co^{2+}-Zr^{4+}$ [18], $Mn^{2+}-Co^{2+}-Zr^{4+}$ [19], $Zn^{2+}-Ti^{4+}$ [20], $Zn^{2+}-Sn^{4+}$ [21], $Zn^{2+}-Mo^{4+}$ [22], $Co^{2+}-Zr^{4+}$ [23] etc. has also been substituted in different types of ferrites in the literature. It has been observed that compared to single ions substitution a combination of divalent and tetravalent ions affect greatly to improve the magnetic properties in particular. $Zn^{2+}-Zr^{4+}$ ions could be an effective combination while considering that Zn ions can occupy the tetrahedral site and Zr ions to occupy octahedral site. The divalent ion of zinc (Zn²⁺) as a substitution showed interesting fundamental properties improvement in ferrites in various applications [24,25]. The published work also showed that the

substituted tetravalent ions has increased the resistivity of ferrites [3, 26].

Preparation techniques also play a major role while governing the properties of ferrites [1]. Sol-gel auto-combustion method has been used in the present work to synthesize the materials, since this method require less time i.e. fast processing time, lower temperature and also prepare materials in nanometer dimension [1,27–29]. In the present work, Zn^{2+} and Zr^{4+} substituted CoFe₂O₄ with a chemical composition of CoZn_xZr_xFe_{2-2x}O₄ (x = 0.0 to 0.4 in step 0.1) has been synthesized by sol-gel method to investigate its structural and magnetic properties.

2. Experimental procedure

The sol-gel method was used for the preparation of $CoZn_xZr_xFe_{2.2x}O_4$ (x = 0.0 to 0.4) ferrite. The nitrates used for preparation of cobalt ferrite are; iron nitrate (Fe(NO₃)₃·9H₂O), cobalt nitrate (Co(NO₃)₂·6H₂O),



Fig. 1. Chemical reaction of CoZn_xZr_xFe_{2-2x}O₄ Ferrites.

zirconium nitrate (Zr(NO₃)₂·xH₂O) and zinc nitrate (Zn(NO₃)₂·6H₂O). All these nitrates were of 99.9% pure bought from Alfa Aesar and Sigma Aldrich. The molar ratio of metal nitrates to citric acid (as a fuel) was kept as 1:2 and was dissolved in double distilled water. This solution was thoroughly mixed using magnetic stirrer for 30 min. The neutral solution (pH ~7) was made by dropwise addition of liquid ammonia. The solutions were heated continuously on a magnetic stirrer at 100 °C to till the solution turn in to gel. The gel was further kept heating without magnetic stirrer till combustion took place followed by the formation of nanostructured powder. The as-prepared powder was annealed at 650 °C for 5 h in the muffle furnace in an air atmosphere. Fig. 1 represents the chemical reaction of prepared samples.

Structural analysis of the selected samples was completed using Xray ray diffractometer (XRD), Philips X'Pert instrument (Cu–K α radiation, $\lambda = 1.54056$ Å). The morphological study of prepared samples was done with the transmission electron microscopy (Model CM 200). Vibrating sample magnetometer (VSM 4500) and Commercial PARC EG are used to study magnetic properties with 1T magnetic field. Room temperature Mössbauer spectra were studied with Mössbauer spectrometer (Nucleonix Systems Pvt. Ltd., Hyderabad, India). The velocity scale calibration was done with α -⁵⁷Fe metal foils.

3. Results

3.1. Structural properties

The X-ray diffraction pattern of cobalt ferrite nanoparticles substituted with Zn-Zr is presented in Fig. 2. FULLPROF software was used for refinement of the prepared samples. Table 1 represents the refined parameters that includes, values of goodness fit factor (χ^2), expected R factor (R_{exp}) and weighted profile R-factor (R_{wp}). CoZn_xZr_xFe_{2-2x}O₄ (x = 0.0) forms single cubic phase cubic spinel structure. The main reflection peaks (220), (311), (400), (422) (511) and (440) corresponding to cubic spinel structure are observed in all the prepared samples. However, α -Fe₂O₃ hematite phase [30] is formed for samples doped for x > 0.2. Apart from these hematite phase some peaks related to the ZrO₂ like monoclinic and tetragonal phases with planes (111) and (220), (140) respectively were observed [31].

The equation used to obtain experimental lattice parameter (a_{exp}) was as below.



Fig. 2. Rietveld refined XRD patterns of $CoZn_xZr_xFe_{2-2x}O_4$ ferrites. Tetragonal and monoclinic phases of ZrO2 are denoted by '*' and '# 'symbols respectively, where α -Fe₂O₃ phase is marked with '+' symbol.

Table 1

Discrepancy factor (R_{wp}), expected values (R_{exp}), goodness fit factor (χ^2) and particle size (t_{TEM}), bulk density (d_B) and porosity (P) of CoZn_xZr_xFe_{2-2x}O₄.

x	R _{exp}	R _{wp}	χ^2	t _{TEM} (nm)	d _B (g/cm ³)	P (%)
0.0	12.5	12.3	1.03	-	4.215	20.59
0.1	12.6	12.3	1.05	-	4.315	20.00
0.2	12.2	11.6	1.09	45	4.382	19.96
0.3	15.5	11.8	1.73	-	4.525	18.62
0.4	15.0	12.1	1.51	80	4.635	17.83

$$a_{exp} = d_{hkl} \left[h^2 + k^2 + l^2 \right]^{1/2} \tag{1}$$

where (h k l) are the miller indices and d is the lattice spacing between the planes. The variation of a_{exp} with $Zn^{2+}-Zr^{4+}$ substitution is shown in Fig. 3a. The Nelson–Riley function F(θ), for each reflection of the studied nanoferrites was obtained from the equation:

$$F(\theta) = \frac{1}{2} \left[\left(\frac{\cos^2 \theta}{\sin \theta} \right) + \left(\frac{\cos^2 \theta}{\theta} \right) \right]$$
(2)

Nelson–Riley plots are shown in Fig. 3b for all the prepared samples. Extrapolating Nelson–Riley function $F(\theta) = 0$ or $\theta = 90^{\circ}$ gives the correct lattice parameter ao values. It is seen from Fig. 3 a and b that as the substitution of $Zn^{2+}-Zr^{4+}$ increases, lattice parameter also increases. This is due to fact that Fe^{3+} ions which have smaller ionic radii (0.67 Å) are replaced by Zr^{4+} and Zn^{2+} ions having greater ionic radii 0.80 Å and 0.83 Å respectively [32,33]. For all synthesized samples the X-ray density (d_x) was calculated from the equation:

$$d_x = \frac{8M}{Na^3} \tag{3}$$

where N is Avogadro's number, M is molecular weight and *a* is the experimental lattice parameter Fig. 3a reveals x-ray density values. Similar to lattice parameter, x-ray density also increased with the Zr^{4+} and Zn^{2+} substitution as shown in Fig. 3a. It is because the Fe ions are smaller than $Zn^{2+}-Zr^{4+}$ ions. Average crystallite site (D_{xrd}) was estimated from the most intense peak (311) of XRD pattern and by employing Scherrer method [34]:

$$d_{xrd} = \frac{0.9\lambda}{B\cos\theta} \tag{4}$$

where, d_{xrd} is crystallite size, λ is wavelength of x-ray, B is full-width of half maxima of XRD peak taken for calculation and θ is position of XRD peak in degree. As observed from Fig. 3c that the values of crystallite site are in nanometer range. The specific surface area (*S*) in g/cm³ was obtained from the relation as discussed in elsewhere [35]. As the composition of Zr⁴⁺ and Zn²⁺ increases also particle size increases and hence there is decrease in specific surface area (Fig. 3c). Bulk density (dB) and porosity (P) of the prepared samples were measuremed using the equation discussed elsewhere [32]. It is observed from Table 1 that bulk density increased from 4.215 to 4.635 g/cm³, whereas percentage porosity decreased from 20.59 to 17.83 with the increase in Zr⁴⁺ and Zn²⁺ substitution. The variation in bulk density and porosity is related to the increase in particle size with the increase in Zr⁴⁺ and Zn²⁺ substitution. The hopping lengths for tetrahedral A-site (*L_A*) and octahedral B-site (*L_B*) were calculated using the equations [36].

$$L_A = a \sqrt{\frac{3}{4}} \tag{5}$$

$$L_B = a \sqrt{\frac{2}{4}} \tag{6}$$

Fig. 3d shows hopping lengths, L_A and L_B for tetra- and octa-hedral, respectively. It is observed that as content of $Zn^{2+}-Zr^{4+}$ in cobalt ferrite increases, hopping lengths also increases and this is due to deviation in



Fig. 3. (a) Experimental lattice parameter (a_{exp}) and X-ray density (d_x) , (b) Nelson–Riley plots to obtain lattice constant (a_0) , (c) crystallite size obtained from xrd (D_{xrd}) and specific surface area (S) and (d) hopping lengths of tetrahedral A-site (L_A) and octahedral B-site (L_B) CoZn_xZr_xFe_{2-2x}O₄ ferrites.



Fig. 4. (a) and (b) TEM images of x = 0.2 and x = 0.4 respectively, (c) and (d) particle size distribution histogram of x = 0.2 and x = 0.4 samples respectively.

ionic radii among Fe³⁺, Zn²⁺ and Zr⁴⁺ ions. The observed variation of hopping lengths with x is in good agreement with the variation of lattice constant with $Zn^{2+}-Zr^{4+}$ substitution. This variation may be attributed to the difference in the ionic radii of the constituent ions, which makes the distance between the ions larger to each other and the hopping lengths increased with $Zn^{2+}-Zr^{4+}$ substitution.

TEM images of selected samples are (x = 0.2 and x = 0.4) shown in Fig. 4 (a and b). At higher Zn-Zr substitution level agglomeration of particles is observed and it may be due to formation of another phase which affects the crystal lattice of cobalt ferrite. Particle size of these samples were obtained by particle size distribution histograms (Fig. 4 c and d). These histogram were obtained by analyzing four TEM images of the respective samples. It is found that the average particle sizes are ~45 nm and ~80 nm for x = 0.2 and x = 0.4, respectively. The increase in particle size with increase in Zn²⁺–Zr⁴⁺ substitution could be related to long growth process.

Shared, unshared octahedral edge (d_{BXE} , and d_{BXEU}), tetrahedral and octahedral bond lengths (d_{Ax} and d_{Bx}) and tetrahedral edge (d_{AXE}) were obtained from the following relations:

$$d_{BXEshaired} = a\sqrt{2} (1 - 2u) \tag{7}$$

$$d_{BXEunshaired} = a \left(4u^2 - 3u + \frac{11}{16} \right)^{\frac{1}{2}}$$
(8)

$$d_{AX} = a\sqrt{3}\left(u - \frac{1}{4}\right) \tag{9}$$

$$d_{BX} = a \left[3u^2 - \left(\frac{11}{4}\right)u + \frac{43}{64} \right]^{\frac{1}{2}}$$
(10)

$$d_{AXE} = a\sqrt{2}\left(2u - \frac{1}{2}\right) \tag{11}$$

where 'u' is oxygen positional parameter and 'a' is the experimental values of lattice constant. The variation of all these allied parameters with Zn–Zr composition is shown in Fig. 5a. It is found that with the substitution of Zn–Zr in cobalt ferrite shared, unshared octahedral edge (d_{BXE} and d_{BXEU}), tetrahedral edge (d_{AXE}), tetrahedral and octahedral bond lengths (d_{Ax} and d_{Bx}) are increased. This variation in allied parameters are related to the change in lattice constant with Zn–Zr composition.

3.2. Cation distribution

CoFe₂O₄ ferrites formed the cubic spinel structure with a chemical formula AB₂O₄, where A referred to the metal cation and is a cubic closepacked crystallography structure consisting 32 anions. It is known that cations in AB₂O₄ occupy two crystallographic sites called tetrahedral A and octahedral B sites [37,38]. In present cobalt ferrite, cation distribution is studied from Rietveld structure refinementof XRD patterns [35]. It can be seen from Table 2 that Zn^{2+} ions occupy the tetrahedral A-site. According to lattice site preference energy, Zr^{4+} ions does not show exact site preference because they have d° configuration. However from earlier work it is evident that Zr^{4+} can occupy both tetrahedral and octahedral sites [39,40]. Even the EXAFS study shows that in certain systems Zr⁴⁺ions occupy tetrahedral site [39]. It is found that from Table 2 that at lower substitution level of Zr⁴⁺ions they are equally distributed among the octahedral and tetrahedral sites while at higher substitution level Zn²⁺ ions drive Zr⁴⁺ ions to the octahedral site. Fe³⁺ ions are present at both tetrahedral and octahedral sites. Using the relation discussed elsewhere [35], and cation distribution



Fig. 5. (a) variation in allied parameters with $Zn^{2+}-Zr^{4+}$ composition, (b) Mean ionic radii at tetrahedral A-site (r_A), octahedral B-site (r_B), (c) theoretical lattice constant (a_{th}) and (d) oxygen positional parameter (u) of $CoZn_xZr_xFe_{2-2x}O_4$.

Atom	$\mathbf{x} = 0.0$		x = 0.1		x = 0.2		x = 0.3	x = 0.3		x = 0.4	
	$\mathbf{x} = \mathbf{y} = \mathbf{z}$	Occ.(g)									
Со	0.1250	0.1002	0.1250	0.1008	0.1250	0.1100(3)	0.1250	0.1405(2)	0.1250	0.2204(3)	
Zn	0.1250	0.0000	0.1250	0.0996(2)	0.1250	0.1997(3)	0.1250	0.3000(1)	0.1250	0.3998(2)	
Zr	0.1250	0.0000	0.1250	0.0012(1)	0.1250	0.0399(1)	0.1250	0.0400(2)	0.1250	0.0500(1)	
Fe	0.1250	0.8998(2)	0.1250	0.8062(1)	0.1250	0.6495(2)	0.1250	0.5192(1)	0.1250	0.3291(2)	
Со	0.5000	0.8997(2)	0.5000	0.9999(1)	0.5000	0.8895(2)	0.5000	0.8590(3)	0.5000	0.7793(1)	
Zr	0.5000	0.0000	0.5000	0.0996(1)	0.5000	0.1599(1)	0.5000	0.2599(1)	0.5000	0.3499(1)	
Fe	0.5000	1.1999(1)	0.5000	0.9999(2)	0.5000	0.9503(2)	0.5000	0.8806(1)	0.5000	0.8706(1)	

Values of atomic coordinates (x, y, z) and occupancy (g) determined from Rietveld refinement of XRD pattern of CoZn_xZr_xFe_{2-2x}O₄.

study, the mean ionic radii 'r_B' of octahedral B-site and 'r_A' of tetrahedral A-site are obtained. The variation in mean ionic radius of the B-site (r_B) and of the A-site (r_A) with substitution of Zn²⁺ and Zr⁴⁺, are shown in Fig. 5b. With the substitution of Zn²⁺ and Zr⁴⁺, r_A increases because of an increase in the composition of Zn²⁺ (0.83 Å) ions and decrease in smaller Fe³⁺ (0.67 Å) ions at A site. At the same time Zr⁴⁺ ion replaces Fe³⁺ ions at the octahedral B site and hence r_B is also increased.

Using the values of $R_0 = 1.32$ Å (radius of oxygen ion) and r_A , an oxygen positional parameter 'u' can be estimated [41]:

$$u = \left[(r_A + R_0) \frac{1}{\sqrt{3a}} + \frac{1}{4} \right]$$
(12)

Fig. 5d indicates that 'u' decreases from 0.3837 Å to 0.3886 Å with the Zn-Zr substitution. As reported by many researchers for ideal fcc packing the oxygen positional parameter 'u' should be 0.250 Å rather than 0.375 Å with the origin at the octahedral sites, while u is about 0.375 Å when its origin at tetrahedral sites and crystal structure is centric [42,43]. Using XRD patterns some researcher reported u > 0.375Å for substituted ferrites [43,44], for pure magnetite u = 0.382 Å and for Cd–Zn ferrites u = 0.390 Å [45]. However, in the present study, u is larger than its perfect value of 0.375 Å, because there is a variation in the theoretical and experimental values of X-ray intensity. Generally, in many spinels, u is larger than perfect value 0.375 Å, due to the small displacement of anions and hence there is an expansion in octahedral and tetrahedral interstices. However, in the present study due to the displacement of the anion from the ideal situation expanded tetrahedral interstices are formed and hence u > 0.375. The lattice disturbance was also analysed from the oxygen positional parameter 'u'. From the tetrahedral and octahedral radii (r_A and r_B) the theoretical lattice parameter 'ath' was estimated [46] and is increased with the substitution of Zn^{2+} and Zr^{4+} ions (Fig. 5c).

3.3. Magnetic measurements by VSM

The magnetic properties play a significant role in the application of ferrites. These properties depend upon microstructure, chemical composition, processing conditions and type of the substituents. The variation of magnetization (M) with applied magnetic field (H) for $CoZn_xZr_xFe_{2-2x}O_4$ spinel ferrites is presented in Fig. 6a. Values of saturation magnetization (Ms) and coercivity (Hc) are extracted from the M – H loops and are presented in Fig. 6b. It is seen that magnetic properties of cobalt ferrite are altered by $Zn^{2+}-Zr^{4+}$ ions substitution, where coercivity (Hc) and saturation magnetization (Ms) are decreased as the substitutions level of $Zn^{2+}-Zr^{4+}$ in cobalt ferrite increased. It is known that magnetic nature of cobalt ferrite is especially influenced by Fe³⁺ ions distribution in crystallographic lattice sites. The density of Fe ions in A and B sub lattice and magnetization are decreased because diamagnetic Zn^{2+} and Zr^{4+} ions after substitution in cobalt ferrite occupy tetrahedral and octahedral sites respectively.

As per Néel's molecular-field model [47], the A-B super exchange interaction predominate the intra-sublattice A-A and B–B interactions. Hence total magnetic moment is the sum of the magnetic moments of the A and B sub lattices. From Néel's two sub-lattice model, the magnetic moment per formula unit (n_B) was obtained:

$$n_B^N = \mathbf{M}_B(\mathbf{x}) - \mathbf{M}_A(\mathbf{x}) \tag{13}$$

where M_A and M_B are the A and B sub-lattice magnetic moments in μ_B . The n_B^N (μ_B) values for $CoZn_xZr_xFe_{2-2x}O_4$ were obtained from ionic magnetic moment of Co^{2+} ($3\mu_B$), Zn^{2+} ($0\mu_B$), Fe^{3+} ($5\mu_B$) and Zr^{4+} ($0\mu_B$) ions and using the cation distribution. The net magnetization in cobalt ferrite is decreased due to replacement of Fe^{3+} ions by Zn^{2+} - Zr^{4+} ions, which indicate that there is decrease in magnetization at the A and B -site sublattice. The presence of α -Fe₂O₃ (hematite) and ZrO₂ at higher substitution of Zn^{2+} - Zr^{4+} ions could also degrade the magnetic properties of $CoZn_xZr_xFe_{2-2x}O_4$. α -Fe₂O₃ is a canted antiferromagnetic at room temperature that possess very weak-magnetism. α -Fe₂O₃ phase may also lead to exchange interaction at the interface of ferrite and hematite phase resulted in small magnetization [48,49]. Moreover, ZrO₂ phase known to be paramagnetic at room temperature that also causes to decrease in magnetization of $CoZn_xZr_xFe_{2-2x}O_4$.

Coercivity values for cobalt ferrite and hence magnetocrystalline anisotropy (K₁) are decreased with increase in composition of Zr^{4+} and Zn^{2+} ions since K₁ is greater for Fe³⁺ ions than Zr^{4+} and Zn^{2+} ions. The decrease in Hc with the Zn^{2+} - Zr^{4+} substitution can also be co-related to the variation in particle and grain size. In the present work particle size tend to increase with Zn^{2+} - Zr^{4+} which may lead to increase in grain size



Fig. 6. (a) Variation of magnetization (M) with applied magnetic field (H) and (b) variation of saturation magnetization (Ms) and coercivity (Hc) for $CoZn_xZr_xFe_{2-2x}O_4$ spinel ferrites.

Physica B: Physics of Condensed Matter 596 (2020) 412400

as well. Grain boundaries reduced with the increase in grain size which acts as a pinning centers for the domain wall [50]. Decrease in pinning cernters minimize the energy requirement for the domain wall motion. Thus, magnetic ions switch their magnetic poles easily with the application of smaller magnetic field, resulted in decrease in coercivity with increase in grain size.

3.4. Field cooled (FC) and zero field cooled (ZFC) measurements

Fig. 7 presents zero field cooled and field cooled magnetization curves for 2-300K temperature range at 100 Oe applied field for all the prepared samples. FC-ZFC plots shows deviation among the FC and ZFC curves which is attributed to ferromagnetic behaviour [51]. In the nano-particles cooled through a ZFC process deviation begin from the anisotropy barrier blocking of the magnetization orientation [51]. In magnetization process, at particular temperature magnetization attend maximum value, this temperature is called as blocking temperature (T_B). Such a peak is obtained in ZFC mode because moment of particles is blocked along anisotropy axes. In the present scenario blocking temperature does not vary much with increase in Zn²⁺-Zr⁴⁺ substitution. The large difference observed in FC and ZFC is related to the enhanced coercivity at lower temperature. In ferrites, coercivity is determined by the anisotropy constant. In the present system, Co²⁺ ion assumed to possess higher anisotropy since Fe³⁺ ions does not possess orbital momentum. Co²⁺ ions in the low symmetry coordination possess orbital contribution due to the relevant spin-orbit coupling resulted in single ion anisotropy [52].

The observed magnetization in FC mode decreased continuously with the increase in temperature and Zn^{2+} and Zr^{4+} substitution. The mechanism of decrease magnetization with Zn^{2+} and Zr^{4+} substitution is analogues with the decrease in saturation magnetization, which is discussed in previous section. Increased thermal randomization of magnetic moments caused decrease in magnetization with increase in temperature. At lower temperature canted or triangular magnetic structure is stabilized whereas antiferromagnetic structure existed in collinear ordering of magnetic moments at higher temperature [53]. Canted magnetic structure in spinel ferrites appeared when B–B exchange interaction at octahedral sub-lattice is strong compared to B–O-A super-exchange, where more likely, the magnetic moments of octahedral-B sub-lattice is canted. Thus at low temperature, the $CoZn_xZr_xFe_{2-2x}O_4$ assumed to in antiferromagnetic states with canted magnetic structure. Magnetic structure linearly changed from canted to



Fig. 7. Variation in field cooled (FC) and zero field cooled (ZFC) with temperature of $CoZn_xZr_xFe_{2-2x}O_4$ ferrites.

collinear with the increase in temperature.

3.5. Mössbauer spectroscopy

A room temperature (300K) Mössbauer spectrum of CoZn_xZr_x -Fe_{2-2x}O₄ ferrites for all the synthesized samples are shown in Fig. 8. It is divided into two separately fine clear sextets corresponding to Fe³⁺ at the octahedral [B] as well as at tetrahedral (A) sites. One of the sextets is characteristic of the Fe³⁺ ions resided at octahedral site because of greater hyperfine field and isomer shift in Zeeman pattern. The second sextet is a characteristic of the Fe³⁺ ions resided at tetrahedral site since smaller hyperfine field and isomer shift in Zeeman pattern [37,38,54, 55].

Six finger pattern spectrums were observed which indicates all selected samples are magnetically ordered. Table 3 shows the calculated values of relative intensity (RI), hyperfine magnetic field (H_{hf}), line width (Γ), isomer shift (IS) and quadruple splitting (QS) corresponding to tetrahedral (A) and octahedral (B) sites for all synthesized samples. The line width at tetrahedral site is expanded compared to the octahedral site, which further increase with the Zn²⁺-Zr⁴⁺ substitution at the tetrahedral and well as octahedral sites. An appropriate distribution of Zr^{4+} , Co^{2+} and Fe^{3+} ions at the B-site and the hyperfine fields distribution at the A-site occurred and thus expansion in line width at tetrahedral site is observed [55]. Change is observed in isomer shift with increase in $Zn^{2+}-Zr^{4+}$ ions substitution which means that electron charge density of Fe^{3+} ions was affected with the increase in $Zn^{2+}-Zr^{4+}$ ions substitution. It can be seen from Table 3 that, at the octahedral sites isomer shift is higher than the tetrahedral sites. The CoZn_xZr_xFe_{2-2x}O₄ spinel ferrites having cubic spinel structure and have maximum $Fe^{3+}-O^{2-}$ bond separation at octahedral sites than that of the tetrahedral sites. Thus there is slight overlapping of Fe³⁺ ions orbital at B-sites, resulting in higher isomer shift at octahedral B-site [56–58]. Magnitude of as obtained values of isomer shift may be due to the high spin configuration iron exists in Fe^{3+} valence state [59]. In the present $CoZn_xZr_xFe_{2-2x}O_4$ ferrite system, quadrupole splitting (Table 3) values for hyperfine spectra are very small since commonly cubic symmetry is maintained between Fe³⁺ ions and their surroundings cations and anions.

As per Néel's super-exchange interactions, in cobalt ferrites as the substitutions of Zn²⁺- Zr⁴⁺ ions increased at A- and B-sites there is a change in hyperfine magnetic field is observed (Table 3). Such a change in hyperfine magnetic field can be described according to the Néel's super-exchange interactions [57]. As the Fe³⁺ ions are occupy both A-site and B-site, their interaction with Zn²⁺, Zr⁴⁺ and Co³⁺ ions is possible. Magnetic linkages in, $Fe_A^{3+} - Co_B^{2+}$, $Fe_A^{3+} - O - Fe_B^{3+}$ and $Fe_A^{3+} - Zn_A^{2+}$ are decreased, because in the present study Fe³⁺ ions having 5µ_B magnetic moment are replaced by non-magnetic Zn²⁺-Zr⁴⁺ ions. Thus, with the increase of Zn²⁺-Zr⁴⁺ content hyperfine magnetic field and magnetization are decreased. Similarly secondary phases such as α -Fe₂O₃ and ZrO₂ also decrease the hyperfine magnetic field due to their canted antiferromagnetic and paramagnetic nature, respectively.

Central paramagnetic doublet superimposed on two well-resolved Zeeman split sextets is observed for x=0.3, which is an indication of the partial short-range ordering is existed along with antiferromagnetic ordering. Such double may appeared due to some Fe^{3+} ions being isolated from other magnetic ions [60, 61]. Doublet is more dominant for x=0.4 which is a characteristic of the paramagnetic feature of Zn^{2+} ions. The secondary phases, ZrO_2 and α -Fe_2O_3 also responsible for the appearance of doublet, that decrease the long-range magnetic ordering since higher number of non-magnetic ions were populated around magnetic Fe^{3+} ions.

4. Conclusions

Sol-gel auto combustion method is successfully used to synthesize



Fig. 8. Room temperature Mössbauer spectra of all the samples of CoZn_xZr_xFe_{2-2x}O₄ ferrite system.

CoZn_xZr_xFe_{2-2x}O₄ ferrites nanoparticles at lower sintering temperature. The XRD pattern shows a formation of cubic spinel structure for $x \le 0.2$, where secondary phases of α -Fe₂O₃ are appeared for x > 0.2. From the cation distribution study, it reveals that majority of Zr⁴⁺ ions occupy octahedral site, however small fraction of these ions also occupy tetrahedral site as well. In present study displacement of anion shows u > 0.375 Å and forms expanded tetrahedral interstices. Coercivity and saturation magnetization of cobalt ferrite are decreased with increase in Zn–Zr composition. Magnetization and magnetic linkages in $Fe_A^{3+} - Co_B^{2+}$, and $Fe_A^{3+} - Zn_A^{2+}$ are decreased because of the replacement of magnetic Fe³⁺ ions by non-magnetic Zn²⁺-Zr⁴⁺ ions. As a result at A and B sites, Fe³⁺ ion experience decreased magnetic field. Magnetization results obtained from the VSM and Mössbauer spectroscopy matched well with each other. ZFC-FC graphs show deviation in the FC and ZFC

curve, which attributes ferromagnetic behaviour.

Credit author statement

S. S. Desai: Preparation and characterizations of samples, Writing - original draft. Sagar E. Shirsath: Calculations and analysis of results, Writing - original draft. Khalid Mujasam Batoo: Analysis of results, Writing - original draft. Syed Farooq Adil: Writing - original draft. Mujeeb Khan: Writing - original draft. S. M. Patange: Conceive the research work, Rietveld refinement, Writing - original draft.

Declaration of competing interest

All the authors hereby declare that they do not have any Conflicts of

Table 3

The relative intensity (RI) in percentage, linewidth (I), isomer shift (IS), quadrupole splitting (QS), Hyperfine magnetic field (H_{hf}) and Fitting quality (χ^2) of tetrahedral and octahedral sites of Fe³⁺ ions for CoZn_xZr_xFe_{2-2x}O₄ (x = 0.0, 0.1, 0.2, 0.3 and 0.4) ferrite derived from Mössbauer spectra recorded at room temperature. Isomer shift values are relative to Fe metal foil ($\delta = 0.0 \text{ mm/s}$). Sextet A: Tetrahedral site, Sextet B: Octahedral site.

x	Iron Sites	RI (%)	Γ (mm/s)	IS (mm/s)	QS (mm/s)	H _{hf} (Tesla)	χ^2
0.0	Sextet A	56.79	0.332102 (±0.02450)	0.15912 (±0.00301)	-0.016025 (±0.00475)	49.22154 (±0.01749)	
	Sextet B	43.21	0.36023 (±0.03921)	0.43772 (±0.00628)	0.148612 (±0.01229)	50.248452 (±0.04941)	
0.1	Sextet A	58.55	0.369817 (±0.04594)	0.263995 (±0.00410)	$-0.011570 (\pm 0.00728)$	47.960246 (±0.04925)	1.19
	Sextet B	41.45	0.694491 (±0.08087)	0.341672 (±0.01697)	$-0.065510(\pm 0.03088)$	49.688579 (±0.43506)	
0.2	Sextet A	43.95	0.286968 (±0.03970)	0.265465 (±0.00397)	0.014301 (±0.00769)	46.542426 (±0.05137)	1.21
	Sextet B	56.05	0.773426 (±0.04485)	0.326947 (±0.01238)	$-0.038131 (\pm 0.02337)$	49.413692 (±0.28624)	
0.3	Doublet	0.65	0.486344 (±0.30613)	0.248804 (±0.06177)	0.220520 (±0.20587)		1.26
	Sextet A	37.95	0.230000 (±0.00000)	0.310329 (±0.00836)	0.001764 (±0.01613)	43.774676 (±0.11353)	
	Sextet B	61.40	1.036929 (±0.05963)	0.379229 (±0.02182)	-0.001109 (±0.04148)	44.016382 (±0.37511)	
0.4	Doublet	9.02	0.428724 (±0.01903)	0.348579 (±0.00564)	0.483531 (±0.00949)		0.94
	Sextet A	26.22	0.230000 (±0.0000)	0.265474 (±0.02325)	0.059268 (±0.04536)	42.324537 (±0.30949)	
	Sextet B	64.74	0.801281 (±0.07384)	0.366924 (±0.02303)	0.042567 (±0.04260)	43.280437 (±0.36079)	

Interest.

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