

Estimation of Cation Distribution in $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ Ferrites Using ^{57}Fe Mössbauer Spectroscopy

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Abstract A series of praseodymium-doped $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.02, 0.06$ and 0.10) ferrites were synthesized by solid-state reaction method to study the impact of doping Pr^{3+} ions on the structural and magnetic properties of $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ferrite compositions. The powdered x-ray diffraction studies revealed the presence of peaks corresponding to tetrahedral and octahedral positions, confirming cubic spinel structure in all samples. Vibratory sample magnetometer study revealed changes in microscopic magnetic properties. The net magnetization increased while the coercivity decreased with increase in concentration of Pr^{3+} substitution. ^{57}Fe Mössbauer studies were used to obtain the chemical state of iron and its occupancy to tetrahedral/octahedral site and to estimate the cation distribution of tetrahedral site and octahedral site in all synthesized ferrite compositions. Using the cation distribution of tetrahedral site and octahedral site, an attempt is made to understand the magnetic properties of Pr doped Zn-Mg ferrites.

Keywords: Spinel Ferrite, Chemical state of iron, Cation Distribution, magnetic properties, ^{57}Fe Mössbauer Spectroscopy

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1. Introduction

Spinel system with general formula MFe_2O_4 ; $\text{M} = \text{Fe}^{2+}, \text{Zn}^{2+}, \text{Co}^{2+}, \text{Mg}^{2+}, \text{Mn}^{2+}$ etc. are named as magnetic spinel ferrites. Spinel ferrites are fundamentally important in the study of super paramagnetism by altering the chemical composition [1]. The spinel structure allows substitution of different metal ions resulting into changes in its electric and magnetic properties [2]. The substitution of metal ions can affect the occupancy of Fe^{3+} ions to be either in tetrahedral site A or in octahedral site B and causes a marked difference in the hyperfine fields at ^{57}Fe nuclei present in site A and site B of spinel structure. ^{57}Fe Mössbauer spectroscopy can be used to study the environment surrounding the iron nuclei in spinel ferrite structures [3,4,5,6,7]. In Mössbauer spectroscopy, the precession and the transition between the precession states is faster in comparison to the experimental time scale and hence an average value of magnetic hyperfine field is obtained. This experimental time scale τ_M is of the order of nuclear larmor precession time (nano second) [8].

In the study of magnetic properties, the super paramagnetic blocking temperature T_B is considered as a significant parameter [9]. T_B is the temperature at which the relaxation time is equal to the time scale of the experimental technique is below T_B , the Mössbauer spectra are magnetically split and exhibit magnetic

hyperfine splitting pattern consisting of six line components (sextet) for each iron site in the material. Above T_B , the Mössbauer spectra contain only singlets or doublets. In a broad temperature range, the spectra of magnetic nano particle can also show the superposition of sextets and doublets or singlets due to the distribution of anisotropy energy various (kV).

The relaxation time τ is given as

$$\tau = \tau_0 \exp\left(\frac{KV}{k_B T}\right)$$

Where K is anisotropy constant, k_B is Boltzmann constant, T is temperature and V is the crystallite volume.

In case of very small sized crystallites, the relaxation time τ is less than the larmor precession time τ_L and leads to super paramagnetic relaxation. In spinel ferrites of nano-sized crystallites this super paramagnetic relaxation can occurs. Due to super paramagnetic relaxation, the spinels do not exhibit magnetic hyperfine splitting and instead of magnetic sextet only doublets are expected to be obtained in its Mössbauer spectrum.

In present study, the Pr^{3+} substituted Zn-Mg ferrites were prepared by solid state reaction method and finally were sintered at 1180°C . The structural parameters were determined from the Rietveld fits of x-ray diffraction pattern in all samples. The ^{57}Fe Mössbauer spectroscopic study was carried out to obtain the chemical state of iron in each composition by determining the local environment

of Fe atom. For all samples, the cation distribution of tetrahedral and octahedral sites was estimated from relative amount of iron in tetrahedral and octahedral sites in spinel structure. The estimated cation distribution was then used to study the magnetic interactions in Pr^{3+} substituted $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_2\text{O}_4$ ferrites.

2. Experimental

The solid state reaction method was used to synthesize the as prepared Zn-Mg ferrite [10] and Pr substituted series of $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.02, 0.06$ and 0.10) ferrite compositions. All prepared samples were sintered at 1180°C . The x-ray diffraction studies were carried out at room temperature by using PANalytical X'pert Pro MPD diffractometer of Cu-K α radiation. The diffraction patterns were collected at 2° per minute scanning rate from 10° to 80° range of 2θ . The indexing and refinement of peaks obtained in x-ray diffraction patterns was carried out by using "FullProf programme [11] to calculate several x-ray parameters like lattice constant, crystallite size, x-ray density and lattice strain.

Mössbauer spectra were recorded at room temperature (300K) with a conventional constant acceleration spectrometer using a 10 mCi ^{57}Co source embedded in Rhodium matrix. Details of the experimental set-up were kept similar as reported earlier by Ram et. al. [12]. The Mössbauer absorbers were prepared by sandwiching a thin layer of fine powdered ferrite samples in between two paper discs and tightly covered with cello tape such that the thickness of absorber remains uniform. All spectra showing superposition of quadrupole doublets were computer fitted to resolve them using a least square routine computer program written by Meerwall [13] by assuming each spectrum to be sum of Lorentzians functions. During the curve fitting, the width and intensity of the two halves of a quadrupole doublet were constrained to be equal. The quality of the fit was judged from the value of χ^2 which was obtained close to 1.0 per degree of freedom in most of the cases. However, a deviation in the value of χ^2 has been accepted in some occasion when iterations did not improve the value of χ^2 . The isomer shift (IS) value is reported with respect to the spectrum of standard iron foil of 25 μm thickness. Solid lines in the spectra reported here represent computer fitted curve and dots represent the experimental points.

The magnetic properties of prepared samples were investigated by recording the variation of magnetizing intensity with applied magnetic field by using Vibrating Sample Magnetometer. The magnetic field was applied in the range of -15 kOe to +15 kOe. The microscopic magnetic parameters like saturation magnetization, coercivity, retentivity, etc. have been calculated to understand the magnetic nature of prepared Pr-substituted $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_2\text{O}_4$ ferrites.

3. Results and Discussion

The x-ray diffraction patterns obtained for all synthesized Pr-substituted Zn-Mg ferrites compositions

[14] with chemical formula $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.02, 0.06$ and 0.10) are displayed in figure 1. The absence of additional peak corresponding to impurity phase Fe_2O_3 confirms the formation of single phase cubic spinel structure in all synthesized ferrite compositions. The broadening of diffraction peaks is attributed to the formation of nano sized particles in all samples. The calculated values of lattice constant, crystallite size, x-ray density and lattice strain are listed in Table 1. The lattice constant 'a' was calculated by using the relation

$a = d\sqrt{h^2 + k^2 + l^2}$, here (h,k,l) is the index of the XRD reflection peak and 'd' is the inter-planar spacing [15]. The x-ray density (ρ_x) in all samples has been calculated

by using the formula $\rho_x = \frac{8M}{N_A a^3}$, where M is relative

molecular mass, N_A is Avogadro number and 'a' is lattice constant [15]. The lattice constant obtained in all Pr-substituted samples is less than the lattice constant obtained in pure sample ($x=0$). The variations of lattice constant and crystallite size with increasing Pr concentration in $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ferrites are displayed in Figure 2. From Figure 2, it is seen that in sample for $x=0.02$, the calculated value of lattice constant is 8.3762 Å which is the smallest value among all samples in present study. This decrease in lattice constant with inclusion of Pr^{3+} ions is obvious because the larger ionic radii Pr^{3+} ion (1.13 Å) has preferential occupancy to octahedral site by replacing $\text{Fe}^{3+}/\text{Mg}^{2+}$ ions from octahedral to tetrahedral site. This results into decrease of lattice constant. However, for higher concentration of Pr-substitution, the minor increase in lattice constant from 8.3762 Å ($x=0.02$) to 8.3997 Å ($x=0.10$) can be explained in context to the linear vibration of crystallography parameters when larger sized Pr^{3+} ions incorporates in lattice structure because of all the samples were synthesized at constant temperature and nature of bonding was also same [16].

From Table 1, it can be seen that the x-ray density also increases with increase in the concentrations of Pr substitution. The increase in x-ray density is obvious due to the larger atomic weight of Pr (140.90), which results into an increase in relative molecular mass with increase in concentration of Pr substitution. The crystallite size in all samples was calculated using the Scherer's formula [15]. The calculated average crystallite size has been observed in the range 53.2 nm to 41.7 nm corresponding to the formation of nano-sized crystallites. This decrease in crystallite size with increasing concentration of Pr Substitutions is due to the Pr^{3+} ions which are distributed over the grain boundary and can obstruct the crystal growth [17]. For sample ($x=0.10$) the crystallite size is obtained to be very small (41.7 nm) in comparison to pure sample (53.2 nm). The sharp decrease in crystallite size with increasing concentration of Pr substitution can be attributed to the larger ionic radii of Pr^{3+} ion due to which the Pr^{3+} ion may reside partially at the grain boundary and cause pressure on the grain resulting in to obstruction of the growth of crystal [18]. When Pr^{3+} ions enter the lattice of spinel, the changing lattice parameters also leads to change in lattice strains. From Table 1, it can be seen that lattice strain ' η ' increases with increasing concentration of Pr substitution.

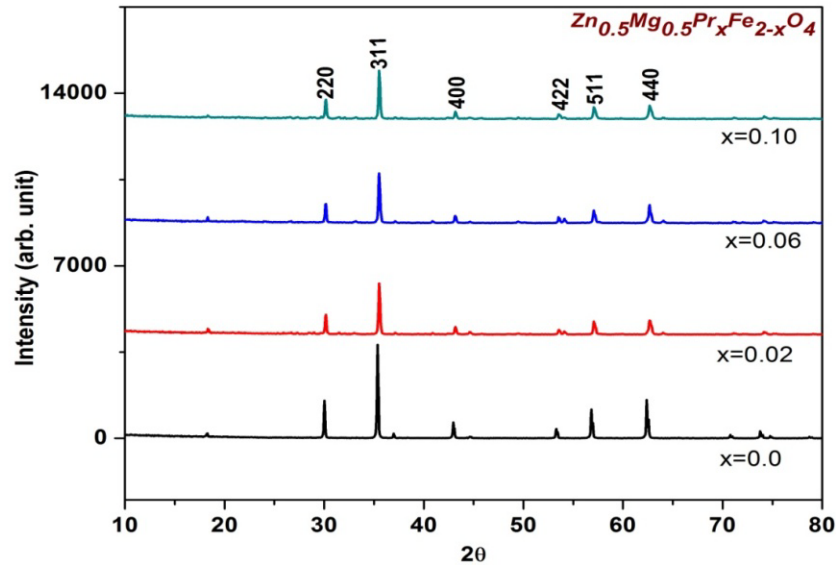


Figure 1. X-ray powder diffraction pattern of $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ferrites [14]

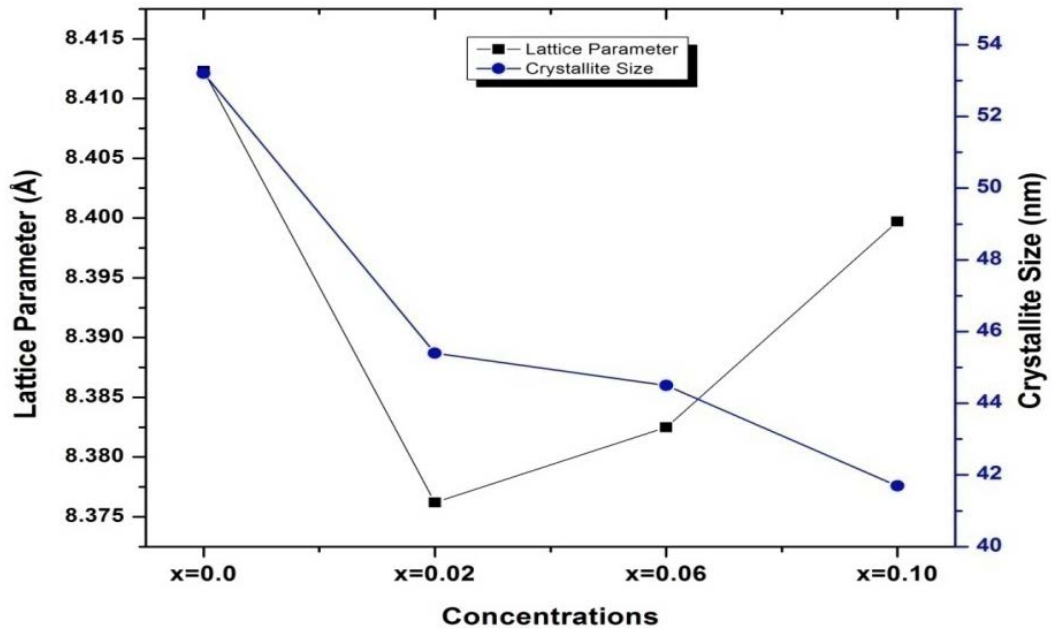


Figure 2. Variations in lattice constant and crystallite size with Pr concentration in $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ferrite

Table 1. Calculated values of X-Ray parameters in $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ferrite with change in Pr concentration

Pr Content (x)	Lattice constant (Å)	Crystallite Size (nm)	X-Ray Density $\rho_x(\text{g/cm}^3)$	Lattice Strain $\eta (\times 10^{-2})$
0.0	8.4123 [9]	53.2 [9]	4.920 [9]	1.048 [9]
0.02	8.3762	45.4	5.022	1.223
0.06	8.3825	44.5	5.088	1.249
0.10	8.3997	41.7	5.151	1.336

The Mössbauer spectra of all synthesized sample recorded at room temperature are displayed in Figure 3. The concentration of Pr^{3+} substitutions is mentioned in the figure itself. The Mössbauer parameters obtained by the least square fitting of Lorentzians lines are given in Table 2. The isomer shift (IS) value is reported with respect to the spectrum of standard iron foil of 25 μm thickness. In present study, the Isomer shift values are

obtained ranging from 0.1 mm/s to 0.4 mm/s which are attributed to iron in Fe^{3+} state [19,20]. The assignment of iron in Fe^{3+} state occupying either tetrahedral site or octahedral site is done in accordance with earlier reported work [7,21,22]. The doublet with higher value of isomer shift is assigned to iron in Fe^{3+} state occupying tetrahedral site-A while the doublet with smaller value of isomer shift is assigned as iron in Fe^{3+} state occupying octahedral site-B.

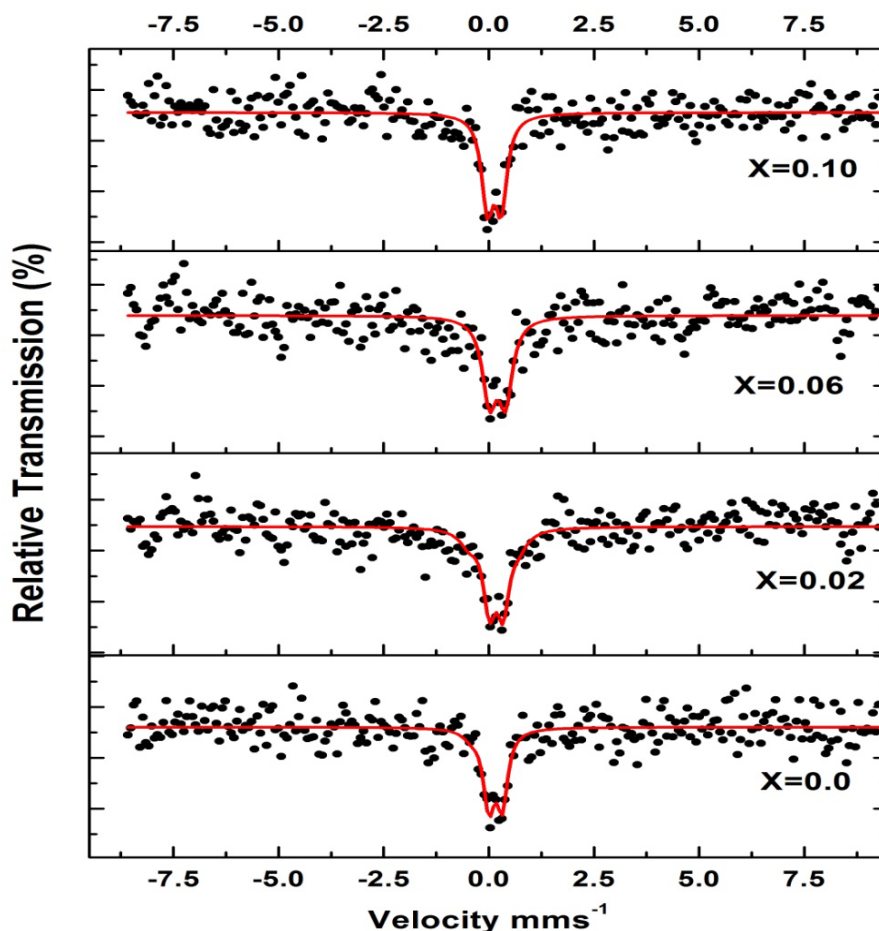


Figure 3. Room temperature Mössbauer spectrum of $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ferrites

Table 2. Mössbauer parameters of $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ferrites

Pr Content (x)	Doublet(s)		IS (mms^{-1})	QS (mms^{-1})	LW (mms^{-1})	RA
0.0	I	Fe^{3+} A-site	0.38	0.20	0.44	24.63
	II	Fe^{3+} B-site	0.13	0.32	0.30	75.73
0.02	I	Fe^{3+} A-site	0.12	1.18	0.51	21.70
	II	Fe^{3+} B-site	0.17	0.32	0.35	78.30
0.06	I	Fe^{3+} B-site	0.20	0.37	0.40	100
0.10	I	Fe^{3+} B-site	0.13	0.32	0.33	100

From Table 2, it can be seen that in pure sample ($x=0.0$) the isomer shift value for site-A is greater than that of site-B. In a similar type of study on Zn-Mn ferrites, Ram and Singh [7] and Wang et. Al. [20] has already reported this trend of larger value of isomer shift for Fe^{3+} iron in site-A. The samples with $x=0.06$ and $x=0.10$ exhibit only one central doublet attributing to the magnetically isolated Fe^{3+} ion which does not show magnetic ordering due to surrounding non magnetic particles [23].

The amount of iron in Fe^{3+} state occupying the tetrahedral site-A and octahedral site-B was estimated by the relative area of the quadruple doublet(s) [24]. In pure sample ($x=0.0$), the distribution of Fe^{3+} ions into site-A and site-B clearly indicate the formation of mixed inverse spinel structure. This formation of inverse spinel Zn-Mg

ferrite ($x=0$) is obvious due to the tendency of divalent ions Zn^{2+} which has preferential occupancy to A-site while Mg^{2+} has preferential occupancy to B-site [25,26].

From Table 2, it can be seen that with increasing concentration of Pr substitution, the relative amount of iron in tetrahedral site reduces and it increases in octahedral site. This clearly reflects the migration of Fe^{3+} ions into octahedral site. The Fe^{3+} ions migrated from tetrahedral site to octahedral site has replaced only Mg^{2+} ions present in octahedral site. It is because Pr^{3+} ions due to their larger ionic radii (1.13 Å) preferentially occupies only octahedral site.

The Mössbauer spectra of samples ($x=0.06, 0.10$) exhibit only one central doublet corresponding to Fe^{3+} iron in B-site only. It shows the complete migration of Fe^{3+}

from tetrahedral to octahedral site by replacement of Mg^{2+} from octahedral site. The tetrahedral site now has only divalent ions Zn^{2+} and Mg^{2+} while the octahedral site has only trivalent ions Fe^{3+} and Pr^{3+} . The cation distribution of tetrahedral site and octahedral site is estimated from Mössbauer spectra in keeping with the earlier reported study by Ram and Singh [7], Singh S. [14] and Mohammed et. al. [27] and is given in Table 3.

Table 3. Cation distribution in $Zn_{0.5}Mg_{0.5}Pr_xFe_{2-x}O_4$ ferrites with different concentration of Pr substitution

Pr Content (x)	A-site	B-site
0.0	$(Zn_{0.5}^{2+} Mg_{0.007}^{2+} Fe_{0.493}^{3+})$	$[Mg_{0.493}^{2+} Fe_{1.507}^{3+}]$
0.02	$(Zn_{0.5}^{2+} Mg_{0.07}^{2+} Fe_{0.43}^{3+})$	$[Mg_{0.43}^{2+} Pr_{0.02}^{3+} Fe_{1.55}^{3+}]$
0.06	$(Zn_{0.5}^{2+} Mg_{0.5}^{2+})$	$[Pr_{0.06}^{3+} Fe_{1.94}^{3+}]$
0.10	$(Zn_{0.5}^{2+} Mg_{0.5}^{2+})$	$[Pr_{0.10}^{3+} Fe_{1.90}^{3+}]$

Using the cation distribution given in Table 3, the average ionic radii at the tetrahedral site (r_A) and at octahedral sites (r_B) in all samples can be calculated by following relations [28]

$$r_A = \left[\frac{C_{Zn^{2+}}^A}{C_{Zn^{2+}}^A + C_{Mg^{2+}}^A} (r_{Zn^{2+}}) + \frac{C_{Mg^{2+}}^A}{C_{Zn^{2+}}^A + C_{Mg^{2+}}^A} (r_{Mg^{2+}}) \right] \quad (1)$$

$$r_B = \frac{1}{2} \left[\frac{C_{Zn^{2+}}^B}{C_{Zn^{2+}}^B + C_{Mg^{2+}}^B} (r_{Zn^{2+}}) + \frac{C_{Mg^{2+}}^B}{C_{Zn^{2+}}^B + C_{Mg^{2+}}^B} (r_{Mg^{2+}}) + \frac{C_{Pr^{3+}}^B}{C_{Pr^{3+}}^B + C_{Fe^{3+}}^B} (r_{Pr^{3+}}) + \frac{C_{Fe^{3+}}^B}{C_{Pr^{3+}}^B + C_{Fe^{3+}}^B} (r_{Fe^{3+}}) \right] \quad (2)$$

Where C^A and C^B are the ionic concentration in A-site and B-sites respectively, $r_{Zn^{2+}}$, $r_{Mg^{2+}}$, $r_{Pr^{3+}}$, and $r_{Fe^{3+}}$, are the radii of Zn^{2+} , Mg^{2+} , Pr^{3+} and Fe^{3+} respectively.

Using the values of radii of tetrahedral site-A (r_A) and radii of octahedral site-B (r_B), the theoretical values of lattice constant a_{th} in all samples can be obtained by the relation [29]

$$a_{th} = \frac{8}{3\sqrt{3}} \left[(r_A + R_0) + \sqrt{3}(r_B + R_0) \right] \quad (3)$$

here R_0 is the radius of oxygen ion ($R_0 = 1.32 \text{ \AA}$)

The calculated values of mean ionic radii of tetrahedral site-A (r_A), mean ionic radii of octahedral site-B (r_B) and calculated value of lattice constant ' a_{th} ' are listed in Table 4.

Table 4. Mean ionic radius of tetrahedral site (r_A) and octahedral site (r_B), theoretical value of Lattice constant (a_{th}), oxygen positional parameter (u) and inversion parameter (δ) in $Zn_{0.5}Mg_{0.5}Pr_xFe_{2-x}O_4$ ferrites

Pr Content (x)	r_A ($\text{\AA}$)	r_B ($\text{\AA}$)	a_{th} ($\text{\AA}$)	u (3/8, 3/8, 3/8,)	δ
0.0	0.705	0.667	8.4163	0.3892	0.0142
0.02	0.704	0.672	8.4281	0.3889	0.0139
0.06	0.700	0.683	8.4513	0.3882	0.0132
0.10	0.700	0.702	8.5019	0.3874	0.0124

It can be seen from Table 4, that the mean ionic radii of r_A and r_B both increases with increase in the concentration of Pr substitution. However, the increase in r_A is very small in comparison to the increase in r_B . The variation in r_A and r_B arise due to difference in the ionic radii of ions present in a particular site [30,31]. The increase in the value of octahedral site mean ionic radii r_B is attributed to the substitution of larger ionic radii Pr^{3+} ion (1.13 $\text{\AA}$) at octahedral site-B by replacing smaller ionic radii Fe^{3+} ions (0.67 $\text{\AA}$). On the other hand, at tetrahedral site-A the Zn^{2+} ions with ionic radii (0.74 $\text{\AA}$) are accompanied either by Mg^{2+} ions having ionic radii 0.66 $\text{\AA}$ or by Fe^{3+} ions of ionic radii 0.67 $\text{\AA}$. At the tetrahedral site-A, due to small difference between the ionic radii of incumbent Fe^{3+} and Mg^{2+} ions, the increase in tetrahedral site mean ionic radii r_A is in small proportion.

From Table 4, it can also be seen that the theoretical value a_{th} and experimental value a_{exp} of lattice constant are nearly same for pure sample ($x=0$) indicating the formation of spinel ferrite with less distortion from cubic structure. However, the difference between a_{th} and a_{exp} values probably incorporates because in the theoretical calculations a closely packed structure of spinel ferrite is considered. In the samples containing Pr substitution, an increase in a_{th} is observed and it further increases with increasing Pr concentration. This larger variation in a_{th} and a_{exp} for higher concentration of Pr substitution is attributed to the distortion from cubic structure which is obvious as the substitution of Pr^{3+} ions with ionic radii (1.13 $\text{\AA}$) larger than the ionic radii of Fe^{3+} ions (0.67 $\text{\AA}$) will exert an internal stress which can cause the distortion from cubic structure.

In present study, the extent of distortion from cubic symmetry has been estimated by calculating the oxygen positional parameter (u) which describe the displacement of oxygen ions considering origin at site-A and assuming centre of symmetry at (3/8, 3/8, 3/8). The deviation of (u) from its standard value ($u_{ideal} = 0.375$) is given by inversion parameter (δ). The oxygen positional parameter (u) and inversion parameter (δ) for all samples was calculated by using the relations [32] and listed in Table 4.

$$u^{43m} = \frac{r_A + R_0}{a_{th}\sqrt{3}} + \frac{1}{4} \quad (4)$$

$$\delta = u - 0.375 \quad (5)$$

In an ideal FCC structure, the origin from site-A to site-B is convertible by using the relation [33]

$$u_{(A-site)} = u_{(B-site)} + 1/8$$

From Table 4, it is seen that the oxygen positional parameter (u) is slightly larger than the ideal value but show a decreasing trend as the concentration of Pr^{3+} substitution in increased. The displacement of oxygen ions in spinel structures is also related to the ratio of largest divalent ion to the smallest trivalent ion [33]. A larger value of this ratio favours larger displacement of oxygen ions and hence larger value of (u) is expected. In present study, the largest divalent ion is Zn^{2+} ion and the smallest

trivalent ion is Fe^{3+} ion. The ratio $\left[\frac{r(Zn^{2+})}{r(Fe^{3+})} \right]$ is obtained

to be larger favouring larger value of (u). The deviation of (u) from its standard value is an indicator of the trigonal distortion at site-B. It is observed in Table 4 that the trigonal distortion at site-B decreases with increasing concentration of Pr substitution. The decrease in the value of inversion parameter (δ) with increasing Pr^{3+} concentration is attributed to the expansion of octahedral interstices to accommodate the Pr^{3+} ions having larger ionic radii. The increasing value of mean ionic radii of octahedral B-site (r_B) is due to this expansion of octahedral interstices. The Pr^{3+} ions have preferential occupancy to octahedral site which already has larger interstices in comparison to tetrahedral site. The larger ionic radii Pr^{3+} ions will cause the increase in bond length at octahedral site. The increase in bond length is an indicator of weakening of super exchange interactions.

The M-H curve obtained in all synthesized samples of $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ferrites, recorded at room temperature in the applied magnetic field range $\pm 15\text{kOe}$ are shown in Figure 4. The calculated magnetic parameters in $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ferrites are listed in Table 5.

The magnetization in all samples showed an increase with increasing magnetic field and attained maximum value at around 15kOe . None of the produced ferrites has attained saturation magnetization. The maximum magnetization also showed an increase with increasing Pr content. A remarkable increase in total magnetization is observed in $x=0.06$ and $x=0.10$ samples. This increase in maximum magnetization can be explained on the basis of cation distribution of tetrahedral site-A and octahedral site-B due to which the magnetization at site-A and site-B is effective.

For nano-sized ferrites, the total magnetization is given as $M_s = M_B - M_A$ [19,34].

Where M_B is magnetization of sub lattice-B and M_A is magnetization of sub lattice-A.

From Table 3, it is evident that in sample ($x=0$) the iron is present in Fe^{3+} state and occupy site-A as well as site-B resulting into net magnetization, the same is also observable in Figure 4. In sample ($x=0.02$) due to the partial migration of Fe^{3+} ions from site-A to site-B, an increase in magnetization at site-B and simultaneous decrease in magnetization at site-A has resulted in to an increase in net magnetization. In samples ($x=0.06$ and $x=0.10$) the increase in total magnetization is obvious because the cation distribution indicates the occupancy of Fe^{3+} ions only in site-B. The non occupancy of Fe^{3+} ions in site-A results into zero magnetization in site-A because

the other divalent ions Zn^{2+} and Mg^{2+} present in site-A exhibits zero magnetic moment. This rise in maximum magnetization in samples ($x=0.06$ and 0.10) can be also seen in Figure 4.

The increase in net magnetization can also be explained on the basis of decrease in crystallite size (Table 1) with increasing concentrations of Pr substitution. The smaller grain size leads to larger surface/volume ratio which does not support random canting for particle surface spins and hence reduces anti-ferromagnetic exchange interaction [35]. The larger ionic radii Pr^{3+} ion does not enter the tetrahedral site because the inter planer spaces in tetrahedral site-A is small in comparison to the inter planer spaces in octahedral site-B. The Pr^{3+} ions enter octahedral site by replacing Fe^{3+} ions. The cation distribution of tetrahedral and octahedral sites with increasing Pr-substitution (Table 3) reveals the migration of Fe^{3+} ions to octahedral site-B and Mg^{2+} ions to tetrahedral site-A. It points out that Pr^{3+} ions replaces Fe^{3+} ions at octahedral site and meanwhile Fe^{3+} ions of both tetrahedral and octahedral sites replaces Mg^{2+} ions from octahedral site. The presence of Fe^{3+} ion only in octahedral site will reduce anti-ferromagnetic B-B exchange interaction leading to reduction in spin canting in site-B, hence the increase in magnetic moment of sub lattice-B leads to an increase in net magnetization [36]. The variation of oxygen positional parameter (u) with increasing concentration of Pr-substitution is also indicating the expansion of octahedral interstices to cause weakening of A-B interaction. The variation of saturation magnetization (M_s) obtained in all synthesized Pr-substituted ferrite samples are displayed in Figure 5. The saturation magnetization (M_s) is found to increase with increasing concentration of Pr-substitution. From Table 3, it can be seen that for larger concentration of Pr-substitution, the occupancy of octahedral site by Fe^{3+} ion increases. In samples $x=0.06$ and $x=0.10$ along with Pr^{3+} ions, the Fe^{3+} ions are present only in octahedral site. Since Pr^{3+} ion of larger ionic radii ($1.13\text{\AA}$) has preferred occupancy of octahedral site and accommodates only in octahedral site, the interaction of Fe^{3+} ion with Pr^{3+} ions in the spin down state ($4e$, $4f_1$ and $4f_2$) can enhance the net magnetization [37]. Hence the larger values of net magnetization for increasing Pr concentration indicate that the Fe^{3+} ions in the spin down states have interacted with Pr^{3+} ions. This leads to an increase in net magnetization in upward spin, the magnetic moment also increase resulting into an increase in net magnetization.

Table 5. Magnetic parameters obtained in $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ferrites

Pr Content (x)	H_c (Oe)	M_s (emu/g)	M_r (emu/g)	Remanence Ratio (M_r/M_s)	$K_a = (H_c \times M_s)/0.98$ (erg/cm ³)	μ_B (Bohr Magnetron)
0.0	28.892	15.22	0.6569	0.043	448.7104	0.6009
0.02	21.183	17.20	0.5272	0.030	371.7832	0.6844
0.06	24.332	19.59	0.6970	0.035	486.3917	0.7914
0.10	24.773	20.46	0.7451	0.036	517.1995	0.8390

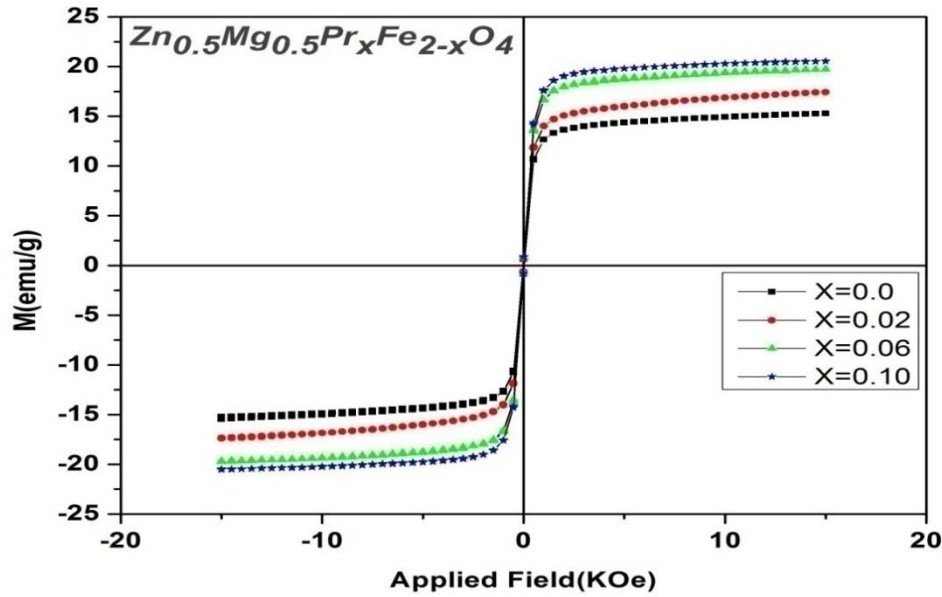


Figure 4. M-H curves for $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ferrites

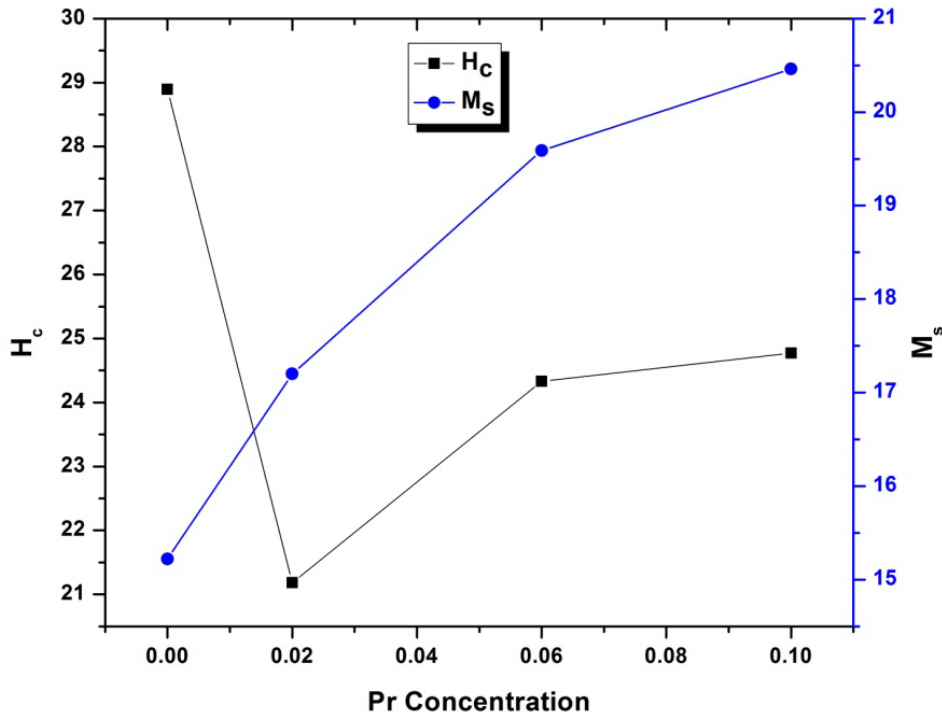


Figure 5. Variation of saturation magnetization (M_s) and coercivity (H_c) with increasing Pr concentration in $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ferrites

The coercivity of as prepared Zn-Mg ferrite sample ($x=0$) is 28.893. The smaller value of coercivity less than 100 Oe indicates that it is a soft magnetic material. From Figure 5, it is seen that coercivity of Pr-substituted samples is obtained to be less than that of pure sample ($x=0$). With increasing Pr-content, the coercivity in sample $x=0.02$ is 21.186 and increases in small proportion with increasing Pr-content and reaches to 24.773 in sample $x=0.10$. Irrespective of the decrease in crystallite size in Pr-substituted samples, the decrease in coercivity in sample $x=0.02$, can be attributed to the larger ionic radii of Pr^{3+} ions due to which it is distributed over the boundary of grain and cause an increase in surface disorder. For further increasing the Pr concentration, the surface disorder also increases and hence rise in coercivity

is expected. In an earlier work, Yuping et. al. [38] and Shirsath et. al. [39] has also reported the increase in coercivity with rare earth doping.

4. Conclusions

Rare earth Pr^{3+} ions substituted $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Pr}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0.0, 0.02, 0.06$ and 0.10) ferrites were successfully synthesized by solid state reaction method. Various structural parameter studied by using x-ray diffraction patterns confirmed the formation of single phase cubic structure in all samples. The Lattice constant as well as x-ray density increased with substitution of Pr^{3+} ions in Zn-Mg ferrites. The crystallite size was obtained in

decreasing trend i.e from 53.2 nm ($x=0$) to 41.7 nm ($x=1.0$), attributing to the formation of nano-sized crystallites. ^{57}Fe Mössbauer spectra of all sample reflected super paramagnetic nature attributing to the formation of nano structured spinel ferrites. The super paramagnetic behavior points towards the non magnetic ordering by Fe^{3+} ions surrounded by non metallic particles. The synthesized nano-sized ferrites with increasing concentration of Pr^{3+} ions exhibit enhanced net magnetization and smaller value of coercivity indicating the soft magnetic behavior of all samples.

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Declaration

The manuscript has been prepared through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors declare that they have no conflicts of interest.

References

- [1] Henderson, C. M. B., Charnock, J. M. and Plant, D. A., (2007), Cation occupancies in Mg, Co, Ni, Zn, Al ferrite spinels: A multi-element EXAFS study, *J. Phys. : Condens. matter*, Vol. 19 (7), 076214.
- [2] Ahamed, T., Rahman, I. Z. and Rahman, A., (2005), Study on the properties of the copper substituted NiZn ferrites, *J. Mater. Process. Tech.*, Vol. 153, pp. 797-803.
- [3] Mahmoud, M. H. and Sattar, A. A., (2004), Mössbauer study of Cu-Zn ferrite substituted with rare earth ions, *J. Magn. Magn. Mater.*, Vol. 277 (1-2), 101-105.
- [4] Meng, X., Li H., Chen, J, Mei, L., Wang, K. and Li, X., (2009), Mössbauer study of cobalt ferrite nanocrystals substituted with rare earth Y^{3+} ion, *J. Magn. Magn. Mater.*, Vol. 311(9), pp. 1155-1158.
- [5] Routray, K., Saha, S. and Behera, D., (2019), Rare-earth (La^{3+}) substitution induced changes in the structural, dielectric and magnetic properties of nano- CoFe_2O_4 for high-frequency and magneto-recording devices, *Appl. Phys. A.*, Vol. 125(5).
- [6] Routray, K., Saha, S., Sanyal, D. and Behera, D., (2018), Role of rare-earth (Nd^{3+}) ions on structural, dielectric, magnetic and Mössbauer properties of nano- CoFe_2O_4 : useful for high frequency application, *Mat. Res. Exp.*, Vol. 6(2).
- [7] Ram, S. and Singh, S., (2022), Study of magnetic interactions in Dy^{3+} substituted $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Dy}_x\text{Fe}_{2-x}\text{O}_4$ Ferrites, *World J. Chem. Edu.*, Vol. 10(2), pp. 76-83.
- [8] Mørup, S. and Hansen, B. R., (2005), Uniform magnetic excitation in nanoparticles, *Phys. Rev. B (Cond. Matter & Materials Phys.)*, Vol. 72(2), 024418.
- [9] Brown Jr., W. F. (1963), Thermal fluctuations of a single-domain particle, *Phys. Rev.*, Vol. 130, 1677-1686.
- [10] Singh, S, Barbar, S. K. and Ram, S., (2018), Synthesis and Characterization of Zn-Mg Ferrite, *AIP Conf. Proc.*, 1953, 090023.
- [11] Rodriguez-Carvajal, B., (2001), Recent developments of the program FULLPROF, commission on powder diffraction, *IUCr. Newsl.*, Vol. 26.
- [12] Ram, S., Patel, K. R., Sharma, S. K. and Tripathi, R. P. (1998) Distribution of iron in siderite in sub-surface sediments of Jaisalmer Basin (India) using Mössbauer spectroscopy, *Fuel*, v. 77, No 13, pp. 1507-1512.
- [13] Meerwall, E.von., (1975), A least-squares curve fitting routine for strongly overlapping Lorentzians or Gaussians, *Comp. phys. Comm.*, Vol. 9(2), pp.117-128.
- [14] Singh S., (2022), Study of structural, magnetic and electric properties of ferrite nanoparticles doped with rare earth elements, <http://hdl.handle.net/10603/454821>.
- [15] Cullity, B. D. and Stock, S. R., (2001), *Elements of X-ray diffraction*, Third Ed. Prentice-Hall, New York.
- [16] Smallman, R.E., (1985), *Modern physical metallurgy*, fourth Ed., Butterworths-Heinemann, London.
- [17] Pachpinde, A. M., Langade, M. M., Lohar, K. S., Patange, S. M. and Sagar, E. S, (2014), Impact of larger rare earth Pr^{3+} ions on the physical properties of chemically derived $\text{Pr}_x\text{CoFe}_{2-x}\text{O}_4$ nanoparticles, *Chem. Phys.*, Vol. 429, pp. 20-26.
- [18] Mohseni, H., Shokrollahi, H., Sharifi, I. and Gheisari, K., (2012), Magnetic and structural studies of the Mn-doped Mg-Zn ferrite nanoparticles synthesized by the glycine nitrate process, *J. Magn. Magn. Mater.*, Vol. 324, no. 22, pp. 3741-3747.
- [19] Kumar, S., Farea, A. M. M., Batoo, K. M., Lee, C. G., Koo, B. H. and Yonsef, A., (2008), Mössbauer studies of $\text{Co}_{0.5}\text{Cd}_x\text{Fe}_{2.5-x}\text{O}_4$ ($0.0 \leq x \leq 0.5$) ferrite", *Physica B: Condensed matter*, Vol. 403 (19-20), pp. 3604-3607.
- [20] Eltabey, M. M., Massoud, A. M. and Radu, C., (2014), Microstructure and Superparamagnetic Properties of Mg-Ni-Cd Ferrites Nanoparticles, *Journal of nanomaterials*, Vol. 204, pp. 492832.
- [21] Wang, J., Zeng, C., Peng, Z. and Chen, Q., (2004), Synthesis and magnetic properties of $\text{Zn}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ nanoparticles, *Physica B*, Vol. 349 (1-4), pp. 124-128.
- [22] Sreeja, V., Vijayanand, S., Deka, S. and Joy, P., (2008), Magnetic and Mössbauer spectroscopic studies of NiZn ferrite nanoparticles synthesized by a combustion method, *Hyperfine interaction*, Vol. 183(1-3), pp. 99-107.
- [23] Gupta, M. and Randhawa, B. S., (2011), Mössbauer, magnetic and electric studies on mixed Rb-Zn ferrites prepared by solution combustion method, *Mat. chem. and phys.*, Vol. 130, pp. 513-518.
- [24] Suwalka, O., Sharma, R. K., Sebastian, V., Laxmi, N. and Venogopalan, K., (2007), A study of nanosized Ni substituted Co-Zn ferrite prepared by coprecipitation, *J. Magn. Magn. Mater.*, Vol. 313, pp. 198-203.
- [25] Thummer, K. P., Chhantbar, M. C., Modi, K. B., Baldha, G. J. and Joshi, H. H., (2004), Localized canted spin behavior in $\text{Zn}_x\text{Mg}_{1.5-x}\text{Mn}_{0.5}\text{FeO}_4$ spinel ferrite system, *J. Magn. Magn. Mater.*, Vol. 280(1), pp. 23-30.
- [26] Phor, L., Chahal, S. and Kumar, V., (2020), Zn^{2+} substituted superparamagnetic MgFe_2O_4 spinel-ferrites: Investigation on structural and spin-interactions, *J. Adv. Ceram.*, Vol. 9(5), pp. 576-587.
- [27] Mohammed, K. A., Al-Rawas, A. D., Gismelseed, A. M., Setlai, A., Widatallah, H. M., Yousif, A., Elzain, M. E. and Shongwe, M., (2012), Infrared and structural studies of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites, *Physics B*, Vol. 407, pp. 795-804.
- [28] Globus, A., Pascard, H. and Cagan, V., (1977), Distance between magnetic ions and fundamental properties in ferrite, *J. Phys. Colloques*, Vol. 38, pp. 163-168.
- [29] Mazen, S. A., Abdallah, M. H., Sabrah, B. A., and Hashem, H. A. M., (1992), The Effect of Titanium on Some Physical Properties of CuFe_2O_4 , *Physica Status solidi (a)*, Vol. 134(1), pp. 263-271.
- [30] Chouhan, B. S., Kumar, R., Jadhav, K. M. and Singh, M., (2004), Magnetic study of substituted Mg-Mn ferrites synthesized by citrate precursor method, *J. Magn.Magn. Mater.*, Vol. 283, pp. 71-81.
- [31] Kumar, G., Kanthwal, M., Chauhan, B. S. and Singh, M., (2006), Cation distribution in mixed Mg-Mn ferrites from X-Ray diffraction technique and saturation magnetization, *Ind. J. Pure & Appl. Phys.*, Vol. 44, pp. 930-934.
- [32] Zaki, H. M., Al-Heniti, S. H. and Elmosalami T. A., (2015), Structural. magnetic and dielectric studies of copper substituted nano-crystalline spinel magnesium zinc ferrite, *J. Alloys and compounds*, Vol. 633, pp.104-114.
- [33] Lakhani, V. K., Pathak, T. K., Vasoya, N. H. and Modi, K. B., (2011), Structural parameters and x-ray Debye temperature determination study on copper-ferrite-aluminates, *Solid State Sciences*, Vol. 13, pp. 539-547.

- [34] Babic-Stojic, B., Jokanovic, V., Milivojevic, D., Jaglicic, Z., Makovec, D., Jovic, N. and Marinovic-Cincovic, M., (2013), Magnetic and Structural Studies of CoFe_2O_4 Nanoparticles Suspended in an Organic Liquid, *Jour. Nanomater.*, Vol. 2013, pp. 741036.
- [35] Pankhurst, Q. A. and Pollard, R. J., (1991), Origin of the spin-canting anomaly in small ferrimagnetic particles, *Physics Review Letters* Vol. 67(2), pp. 248-250.
- [36] Venkataraju, C., Sathishkumar, G. and Shivakumar, K. (2010), Effect of cation distribution on the structural and magnetic properties of nickel substituted nanosized Mn–Zn ferrites prepared by co-precipitation method, *J. Magn. Magn. Mater.*, Vol. 322(2), pp. 230-23.
- [37] Singh, C., Narang, S. B., Hudiara, I. S., Bai, Y. and Tabatabaei, F., (2008), Static magnetic properties of Co and Ru substituted Ba–Sr ferrite, *Mater. Res. Bull.*, Vol. 43(1), pp. 176-184.
- [38] Yuping, W., Lianchao, Li., Hui, L., Haizhen, Q. and Feng, X., (2008), Magnetic properties and microstructure of La-substituted BaCr-ferrite powders, *Materials Lett.*, Vol. 62, pp. 2060-2062.
- [39] Shirsath, S. E., Jadhav, S. S., Toksha, B. G., Patange, S. M. and Jadhav, K. M., (2011), Influence of Ce^{+4} ions on the structural and magnetic properties of NiFe_2O_4 , *J. Appl. Phys.*, Vol. 110, 013914.



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