CHAPTER-4

PART-A

Observation of enhanced magnetic pinning in Sm$^{3+}$ substituted nanocrystalline Mn-Zn ferrites prepared by solution combustion method
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**PART-A**

In the previous chapter, I have been observed that, all the structural and magnetic properties were decreasing with increasing Zn$^{2+}$ content. In this chapter we optimise Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ composition for betterment of properties hence we substitute Samarium at Fe site to optimised Mn-Zn ferrites were successfully synthesized by propellant chemistry route using a mixture of fuels (urea and glucose). The effect of Sm$^{3+}$ ion substitution on the structural and magnetic properties of these ferrites was studied at room temperature. Magnetic properties such as saturation magnetization ($M_s$), remanence ($M_r$) and magneton number ($\eta_B$) were found to decrease, while the coercivity ($H_c$) and reduced remanence ($Mr/Ms$) of the samples were found to increase with increasing Sm$^{3+}$ content. The increase in $H_c$ with increase in Sm$^{3+}$ concentration is interpreted as the enhanced pinning of the magnetic moments at the magnetic defects created by Sm$^{3+}$ ions, which is further confirmed by Mössbauer spectroscopy through a nearly constant magnetic hyperfine field. This results in an increase in the magnetic particle size in spite of decreasing average crystallite size. Our work suggests that, Sm$^{3+}$ substitution can be used to alter the magnetic hardness of Mn-Zn ferrites and to enable them to be used as potential materials for various technological applications.
CHAPTER-4

PART-A

4.1 Motivation

The Mn-Zn nano-ferrites possess excellent magnetic and electric properties, in particular, high permeability, high saturation magnetization, high resistivity and low power loss [1-4]. A lot of emphasis has been given to study the properties of rare earth ion substituted Mn-Zn ferrites as potential candidates for use in magneto-optical devices that require high saturation magnetization, high coercivity and high anisotropy constant [5]. In particular, the substitution of Sm$^{3+}$ ions at the Fe$^{3+}$ site are known to produce very interesting physical and chemical properties in spinel ferrites [6-11]. In view of the wide potential for technological applications such as, wide band microwave absorption [12], magneto-acoustics [13], magneto-caloric pumping [14, 15], temperature sensitive ferrofluids [16], heat-exchange devices [17, 18, 19, 20] we take up the Sm-substituted Mn-Zn ferrites in the present study.

4.2 Results

4.2.1 Structure analysis by XRD

The Rietveld refinement performed on the XRD (Fig. 4.1) data of selected samples with Sm content $y = 0$, 0.01, 0.03 and 0.05, revealed that all the samples have single phase cubic spinel structure (space group $Fd\bar{3}m$). The observed lattice parameter for the undoped sample $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ was 8.4344 Å. This value was significantly lower than the reported value of 8.4510 Å for bulk $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ [21]. This shrinkage in lattice parameter can be attributed to two different factors: (a) change of lattice parameter and cation occupancy due to size effect (nano-size); (b) possible redistribution of cations in the octahedral and tetrahedral interstitial sites [22, 23]. The average crystallite size and lattice strain calculated by using Williamson-Hall method (Table I) showed that the crystallites in our Mn-Zn ferrite sample were nanosized (~17.5 nm). Hence, the observed lower lattice parameter for nanocrystalline Mn-Zn ferrites is in accordance with the literature values [22, 23]. Furthermore, we found that the undoped sample, $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, is a mixed cubic spinel. Refinement of cation occupancies showed that Zn$^{2+}$ were found to be present only in the A site. Neutron diffraction studies [24], Mössbauer spectroscopy studies [25] and site-preference calculations [26] support our finding that Zn$^{2+}$ ions with zero magnetic moment
have a strong preference to occupy the tetrahedral (A) site. However, Mn$^{2+}$ was found to be
distributed over both interstitial sites with a preference to occupy the A site [27], while Fe$^{3+}$
was mostly present in the B site, but a fraction occupying the A site was observed (Table II).
The occupancy of smaller Fe$^{3+}$ ion (radius: 63 pm) in tetrahedral site in place of bigger Mn$^{2+}$
ions (radius: 80 pm) effectively reduces the lattice parameter.

For the Sm-substituted ($y = 0.03$ and 0.05) samples, the lattice parameters (Table I)
showed an appreciably lower value when compared to the unsubstituted ($y = 0.0$) sample.
The lattice parameter of the sample with $y = 0.01$ was comparable to the unsubstituted
sample. The sample with $y = 0.05$ showed an appreciable increase in lattice parameter
compared to the sample with $y = 0.03$. This observation can be explained by considering the
occupancy of Sm$^{3+}$ ions in the octahedral interstitials of the spinel. The Rietveld refinement
of occupancies of Fe$^{3+}$ and Sm$^{3+}$ showed that Sm$^{3+}$ ions occupy only the B site of the spinel,
in all the samples. The refinement of occupancy of Zn$^{2+}$ showed no significant changes from
its preferred A-site occupancy. Due to the preferential occupancy of Sm$^{3+}$ in the B site, there
is rearrangement of (Mn$^{2+}$ and Fe$^{3+}$) cations within the interstitials. The lattice parameter
variation due to this rearrangement could be understood as follows. The variation in lattice
parameter with Sm$^{3+}$ substitution does not follow Vegard’s law. Two competing factors are
responsible for this behavior (i) the mismatch between the ionic radii of the cations and the
size of interstitial sites; and (ii) the charge (valency) differences between the cations. The
tetrahedral site, being smaller (lower bond length and strong interaction), is sensitive to any
small changes in the ionic sizes of the atoms positioned within the site. Octahedral site, on the
other hand, is bigger and bond strength is lower, wherein the occupancy of ions of different
ionic sizes will show up its effect progressively, e.g., with substitution of Sm$^{3+}$ ions. From the
Rietveld refinement results of cation occupancies, we have observed that substitution of Sm$^{3+}$
ions (radius: 107.9 pm) [28, 29] in the B site resulted in a proportional displacement of Fe$^{3+}$
ions (radius: 63 pm) [29, 29] to the tetrahedral (A) site, thereby, proportionally displacing
Mn$^{2+}$ ions (radius: 81 pm) [28, 29] to the octahedral (B) site. For smaller concentrations of the
dopant (Sm$^{3+}$) (i.e., for samples with $y = 0.01-0.03$), the effect of difference in ionic sizes of
cations and their valencies in A-site dominates, reducing the lattice parameter of the sample
(as Fe$^{3+}$ has smaller ionic radii compared to Mn$^{2+}$). However, for the sample with $y = 0.05$,
we speculate that the presence of more Mn$^{2+}$ and Sm$^{3+}$ in B site, which have larger ionic sizes
than Fe$^{3+}$, has more effect on the lattice parameter than the effect of increased number of Fe$^{3+}$
in A-site. The lattice parameter variation with Sm$^{3+}$ content in the sample is shown in Fig. 3
and tabulated in Table I. The maximum error in the estimation of lattice parameter can be in the fourth decimal value. The average crystallite size, evaluated by Williamson-Hall method, was found to decrease with Sm$^{3+}$ content.

![XRD patterns](image)

*Figure 4.1: Rietveld refined XRD patterns for Mn$_{0.9}$Zn$_{0.1}$Fe$_{2+y}$Sm$_{y}$O$_{4}$ samples, $y = 0.0$ (a), 0.01 (b), 0.03 (c) and 0.05 (d). All major reflections are indexed.*

The values of lattice strain were ranging between 0.9-1.0 × 10$^{-3}$ with an increasing trend with Sm$^{3+}$ content. We understood that the substitution of Sm$^{3+}$ in B site might have resulted in increased lattice strain inhibiting the crystallite growth.

From the fit to each Bragg reflection in the Rietveld refined XRD pattern, it can be noticed that there exists an ill-fit to the upper regions of the peaks throughout the pattern (Fig. 4.2). This has repercussions resulting in high value of R-factors (agreement factors) listed in Table I. This misfit may be due to the existence of a wide particle size distribution. To estimate the minimum and maximum crystallite sizes in the sample, the most intense (311) peak, where this ill-fit is more evident, was considered. The (311) peaks of individual patterns was fit by two pseudo-Voigt functions as shown in Fig. 4.2. The FWHM of each pseudo-Voigt plot was taken during the maximum and minimum average crystallite size.
estimation by Scherrer method. The obtained minimum and maximum average particle sizes are listed within the square brackets in Table I.

**Figure 4.2:** Pseudo-Voigt fits to the (311) peak of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_{2+y}\text{Sm}_y\text{O}_4$ samples with $y = 0.0$ (a), 0.01 (b), 0.03 (c) and 0.05 (d).

**Figure 4.3:** Variation of lattice parameter ($a$) with $\text{Sm}^{3+}$ content ($y$) in $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Sm}_y\text{Fe}_{2+y}\text{O}_4$ samples.
Table I. Structural parameters of Mn_{0.5}Zn_{0.5}Fe_{2-y}Sm_{y}O_{4} samples, obtained from Rietveld refinement of XRD data. The values within the brackets represent the minimum and maximum crystallite sizes. “a” is the lattice parameter.

<table>
<thead>
<tr>
<th>y</th>
<th>“a” (Å)</th>
<th>Theoretical Density (g/cc)</th>
<th>X-ray density (g/cc)</th>
<th>Average crystallite size &lt;d&gt; (nm)</th>
<th>Reliability factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rwp</td>
</tr>
<tr>
<td>0.00</td>
<td>8.4344</td>
<td>5.595</td>
<td>5.425</td>
<td>16.2 [9-23]</td>
<td>40</td>
</tr>
<tr>
<td>0.01</td>
<td>8.4292</td>
<td>5.615</td>
<td>5.503</td>
<td>11.0 [5-16]</td>
<td>47</td>
</tr>
<tr>
<td>0.03</td>
<td>8.4215</td>
<td>5.648</td>
<td>5.643</td>
<td>7.9 [3-12]</td>
<td>46</td>
</tr>
<tr>
<td>0.05</td>
<td>8.4346</td>
<td>5.683</td>
<td>5.753</td>
<td>6.2 [3-11]</td>
<td>50</td>
</tr>
</tbody>
</table>

Table II. The cation occupancies at tetrahedral (A) and octahedral (B) sites of Mn_{0.5}Zn_{0.5}Fe_{2-y}Sm_{y}O_{4} samples per formula cell, obtained from the Rietveld refinement of XRD data.

<table>
<thead>
<tr>
<th>y</th>
<th>Cation occupancy mole fraction and (in %)</th>
<th>Sub lattice magnetic moment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn^{2+}</td>
<td>Mn^{2+}</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>0.00</td>
<td>0.5</td>
<td>(100)</td>
</tr>
<tr>
<td>0.01</td>
<td>0.5</td>
<td>(100)</td>
</tr>
<tr>
<td>0.03</td>
<td>0.5</td>
<td>(100)</td>
</tr>
<tr>
<td>0.05</td>
<td>0.5</td>
<td>(100)</td>
</tr>
</tbody>
</table>

4.2.2 Electron Microscopy Results (SEM and TEM)

The SEM micrographs (Fig. 4.5) of the samples show highly porous structures. The structures seem to contain a lot of defects. The appearance of the dry foamy powder is due to the evolution of the gases during the combustion process. As the particle sizes could not be determined from these pictures, we have performed the TEM investigation. The TEM images (Fig. 4.4) reveal that the particle size decreases with Sm^{3+} doping.
The results are consistent with the trend in variation of particle sizes obtained by Williamson-Hall method from the XRD data. However, the observed differences in the absolute values of the average particle sizes could be arising due to the volume occupied by the bigger particles within the experimental volume is large, although the number of such particles is small. This leads to the sharper lines in the XRD (bigger average particle size) but the average number of small particles is more (as seen by TEM).

Figure 4.4: TEM, HRTEM images and particle size distribution for \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Sm}_y\text{Fe}_2\text{O}_4 \) samples, \( y = 0.01 \) (a), 0.03 (b) and 0.05 (c).
4.2.3 FTIR Analysis

Infrared spectra of all the samples (Fig. 4.6) showed two prominent absorption bands, one ($\nu_1$) at $\sim$540 cm$^{-1}$ attributed to the stretching vibration of tetrahedral complexes and the other ($\nu_2$) at $\sim$390 cm$^{-1}$ assigned to the vibration of octahedral complexes. The difference in frequencies between $\nu_1$ and $\nu_2$ is due to the changes in co-ordination number and bond length ($\text{Fe}^{3+}-\text{O}^{2-}$) at tetrahedral and octahedral sites [30, 31]. The slight variation in band intensity from sample to sample may be related to the sample preparation conditions (for the FTIR measurement) and also to the particle size distribution. The band position $\nu_1$ was almost invariant with respect to Sm$^{3+}$ substitution. This supports the XRD result that Sm$^{3+}$ ions occupy the octahedral (B) sites [32].
Figure 4.6: FTIR spectra of Mn$_{0.8}$Zn$_{0.2}$Sm$_{0.5}$Fe$_{2.5}$O$_4$ samples with $y = 0.0$, 0.01, 0.03 and 0.05. The inset shows the zoomed in view of the two band positions (tetrahedral: $\sim$540 cm$^{-1}$ and Octahedral: $\sim$390 cm$^{-1}$)

It can be seen that the absorption band $v_1$ does not show any splitting (shoulders) and hence, the possibility of Fe$^{2+}$ ions at the A-sites is ruled out [31]. On increasing the substitution of the Sm$^{3+}$ ions, $v_2$ should shift slightly towards lower frequency side due to the larger atomic mass and volume of the (Sm$^{3+}$) dopant in comparison to the (Fe$^{3+}$) host, which affects the effective reduced mass on octahedral sites, and hence, the band position. However, due to the limitations of our FTIR spectrometer in observing absorption bands below 400 cm$^{-1}$, the spectra are noisy and no conclusive evidence regarding the occupancy of Sm$^{3+}$ at the octahedral site was obtained.

The peaks observed at $\sim$1300-1700 cm$^{-1}$ are due to the presence of of after combustion carbonaceous residue. The peaks around 2380 cm$^{-1}$ and $\sim$3300 cm$^{-1}$ are attributed to the atmospheric CO$_2$ and -OH stretching vibrations (moisture), respectively.

4.2.4 Magnetic properties by VSM

Fig. 4.7 shows the magnetic hysteresis loops for the samples measured at room temperature with a maximum applied magnetic field of 20 kOe. It is clear that the saturation
magnetization ($M_s$) decreased with increasing Sm-doping. The $M_s$ values of all the samples were obtained as follows: a straight line was extrapolated from the linear region of magnetization curve (i.e., from the high applied magnetic field region, which corresponds to near saturation magnetization of the sample) towards the magnetization axis. The intercept of this line with the magnetization axis was taken as the saturation magnetization $M_s$. The $M_s$ values of all the samples are listed in Table IV. For the undoped Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ sample, a lower value of $M_s$ as compared to bulk was obtained along with a very narrow ‘S-shaped’ hysteresis loop, which suggests the presence of superparamagnetic and single-domain particles. For the Sm-substituted samples, the values of $M_s$ were found to decrease further with increase in Sm-content. This decrease in $M_s$ values might be related to the decrease in size of the nanoparticles as observed from the XRD and TEM results (Table I). This decrease in $M_s$ might also be because, the substituted Sm$^{3+}$ ions have the magnetic moment of 1.58 $\mu_B$ ($\eta_B = 1.58$) [33, 34] which is less than that of Fe$^{3+}$ ($\eta_B = 5\mu_B$) and Mn$^{3+}$ ($\eta_B = 2\mu_B$), at room temperature [33, 34]. Furthermore, the 4f electrons of Sm$^{3+}$ do not have strong exchange interaction with the 3d electrons of Fe$^{3+}$. Hence, the magnetic dipoles (magnetic moments) of Sm$^{3+}$ ions, originating from the 4f electrons, are randomly oriented at room temperature. They are isolated (not strongly interacting with other atoms) and behave as “paramagnetic-like-defect” atoms occupying the B site. This results in a much weaker Mn$^{2+}$-Sm$^{3+}$ (A-B) interaction as compared to the stronger Mn$^{2+}$-Fe$^{3+}$ super-exchange interaction. It can be noticed from Fig.4.8 that for higher Sm$^{3+}$ doping ($y \geq 0.03$), the increasing field branch of the hysteresis loop does not merge with the decreasing field branch. This is a clear indication of the magnetic anisotropy (spin orbit coupling of 3d and 4f-electrons) introduced due to the Sm$^{3+}$ doping. The remanent magnetization ($M_r$) values extracted by the intercept of $M$-$H$ loop on the magnetization axis are listed in Table III. It can be observed that the $M_r$ values were not varying monotonically with Sm-content in the samples. The $M_r$ value for the sample with $y = 0.01$ was the lowest, which suggests that a slight doping of the Sm$^{3+}$ ions the sample shows “higher” superparamagnetic-like behaviour. Higher superparamagnetic behaviour means that the particle-particle interaction becomes negligible. This is also evidenced from the comparison between the Mössbauer spectra of the undoped Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ sample (Fig. 4.8(a)) with the Sm-doped ($y = 0.01$) sample (Fig. 4.8(b)). Here, the area under the broad Zeeman split sextet in Fig. 4.8(a) decreases dramatically and it gives rise to the superparamagnetic-doublet-like spectrum in Fig. 4.8(b). Quantitatively, the average magnetic hyperfine field $<B_{hf}>$ decreases from 24.3 T to 13.0 T (Table III). It was surprising to observe
that the $M_r$ values of the other samples ($y = 0.03$ and $0.05$) are higher, although the saturation magnetization decreases with increasing Sm-content ($y$).

![Graph showing magnetic hysteresis loops for different Sm contents](image)

*Figure 4.7: Magnetic hysteresis loops for Mn$_{0.9}$Zn$_{0.4}$Sm$_y$Fe$_{2.5}$O$_{5}$ samples with $y = 0.0$ (a), 0.01 (b), 0.03 (c) and 0.05 (d).*

Simultaneously, the Mössbauer spectra showed progressive increase in area under the “superparamagnetic-doublet” at the expense of the Zeeman split sextet. Note that this effect is combined with the decrease in particle size and also saturation magnetization.

To understand this aspect better, we considered the quantity “reduced remanence ($S$)” which is the ratio between $M_r$ and $M_s$ values (Eq. 1) of respective samples. Interestingly, as anticipated, the value of the reduced remanence was found to be the lowest for $y = 0.01$ samples and it is higher for higher Sm-doping. However, as observed from Mössbauer spectroscopy, all the samples are superparamagnetic in the Mössbauer spectroscopy time scale of $10^{-8}$s. Had the observed $S$ values originated only from the higher superparamagnetism (due to decreased particle size and reduced particle-particle interaction), we would have observed a monotonic decrease in $S$. Hence, we expect that the observed effect is dominated by the surface pinning and the change in intrinsic magnetic anisotropy of the particles due to Sm-doping.
According to Stoner-Wohlfarth model, the reduced remanence ($S$) of an assembly of non-interacting magnetic particles is given by 0.5 for samples with uniaxial anisotropy and 0.832 for samples with cubic anisotropy [36]. In our samples, the observed values of $S$ for the samples with $y \leq 0.01$ are below 0.5 (Table IV), but for the samples with $y \geq 0.03$, are between 0.5 and 0.7. This suggests that the samples with $y \leq 0.01$ contain bigger non-interacting single domain particles which display uniaxial anisotropy and samples with $y \geq 0.03$ largely contain single domain particles that are not interacting and the observed anisotropy is of the cubic anisotropy type. It is interesting to note that there is a transition from uniaxial anisotropy to cubic anisotropy by doping higher amount of Sm$^{3+}$ at the B-site of Mn-Zn ferrite. As the particle size goes on increasing one should expect to observe an increase in superparamagnetic nature and decrease in the $S$ value. We believe that the observed transition is related to the magnetic anisotropy developed due to Sm-doping. Hence, we have taken Eq. 2(a, b) in the calculation of anisotropy constants ($K_i$ and $K_a$).

Furthermore, in particulate systems, the coercive field ($H_c$) can be originated due to two reasons: (i) inter-particle interactions, and (ii) intra-particle interactions. The intra-particle interactions can be due to surface pinning and bulk magnetocrystalline anisotropy (spin-orbit interaction). From the values of $S$ in our samples, the shape of the hysteresis loops and the Mössbauer spectra, it can be inferred that there exist both inter-and intra-particle interaction. The sample with $y = 0.0$ exhibits very narrow hysteresis loop revealing the soft magnetic behaviour with very weak inter-particle interaction. We expect that these inter-particle interactions for the Sm-doped samples are very weak too and that gradually decrease with increasing Sm-doping and it can be neglected for higher Sm-doped samples. However, in the hysteresis loops of the Sm-doped samples, the coercive field values are found to increase with increasing Sm$^{3+}$ concentration (Table IV) for $y \geq 0.03$, although the particle sizes were found to decrease monotonically (section 3.1). Hence, we expect that the observed behavior is due to pinning of the magnetization at the surfaces of the particles and at the higher amount of magnetic-defects created by increase in Sm-content.

The variation of $H_c$ with particle size can be explained on the basis of domain structure and magnetic anisotropy of the crystallites. The particle size reduction with increasing Sm$^{3+}$ substitution as observed by XRD and TEM results, explains the superparamagnetic behavior present in the samples with increase in Sm content (Table I). With the decrease of particle size, the surface to volume ratio increases and surface effect may induce a spin disorder in the surface layer that causes the spin-pinning to increase with
decreasing particle size and in turn, with increase of Sm$^{3+}$ content. However, it seems that for small amount of Sm-doping ($y \leq 0.01$), the superparamagnetic effect (decreased particle-particle interaction), is enhanced. As the Sm-content increased, the spins within the particles were more strongly pinned than the negligibly weak particle-particle interaction, which enhances $H_e$. The particle-particle interaction is shielded by the pinning due to surface defects.

In our samples, the expected contribution to $H_e$ due to intra-particle interaction is high. As discussed earlier, the contribution to $H_e$ from surface pinning effects and from magneto-crystalline anisotropy is enhanced due to the Sm$^{3+}$ doping. The observed increase in $H_e$ of the higher Sm-doped samples ($y \geq 0.03$) based on magnetocrystalline anisotropy can be understood as below. The magneto-crystalline anisotropy energy associated with an assembly of nanosized particles sample can be estimated from the equation: $E_A = KV \sin^2 \theta$, where, $K$ is the anisotropy energy constant, $V$ is the volume of the particles, and $\theta$ is the angle between the magnetization and easy axis direction. With the increasing magnetic anisotropy, the height of the magnetic anisotropy barrier ($E_A$) increases which requires higher external magnetic field for spin reversal. In pure Mn-ferrite, the magneto crystalline anisotropy is due to the presence of Mn$^{2+}$ ions at the tetrahedral (A) sites of the spinel structure. As we replace Zn$^{2+}$ at the Mn$^{2+}$ site, the amount of Mn$^{2+}$ at the A site decreases and effective magnetic anisotropy of the Mn-Zn ferrite decreases. Thus, the effective magnetic anisotropy and $H_e$ are less for Mn-Zn ferrite, making it a very soft ferrite than pure Mn-ferrite. In the Sm-doped samples, the effective magnetic anisotropy is provided by the A-B exchange interaction between the Mn$^{2+}$ - Fe$^{3+}$, Fe$^{3+}$ - Fe$^{3+}$, Fe$^{3+}$ - Mn$^{2+}$, Mn$^{2+}$ - Sm$^{3+}$ and Fe$^{3+}$ - Sm$^{3+}$, and as discussed earlier, the domain wall pinning of the A-site and B-site Fe$^{3+}$ and Mn$^{2+}$ spins due to Sm$^{3+}$ ion-substitution. The existence of random canting of particle surface spins, surface effects and the occurrence of a magnetic glassy state created by Sm-doping, can play an active role in reducing the saturation magnetization ($M_s$) values and enhancing the coercivity ($H_c$) values.

The magneton number ($\eta_B$) and the Y-K angle ($a_{Y,K}$) were calculated using Eq. 3 and 4, and are listed in Table IV. The value of $\eta_B$ strongly decreased with increase in the Sm-content, which suggests that the obtained $M_s$ values cannot be explained by assuming Néel’s two sub-lattice model for ferrimagnetism. According to Néel’s two sub-lattice model of ferrimagnetism [37], the net magnetic moment per formula unit in ferrimagnetic ferrites is the resultant magnetic moment due to the antiferromagnetic ordering between tetrahedral (A) site and octahedral (B) site magnetic moments. The net magnetic moment is given by the
difference between the A and B sub-lattice magnetic moments: \( \eta_B = M_B(x) - M_A(x) \), where, \( M_A \) and \( M_B \) are the A and B sub-lattice magnetic moments in \( \mu_B \), respectively [40, 41]. However, in our undoped Mn0.5Zn0.5Fe2O4 sample, the presence of non-magnetic Zn\(^{2+}\) ions at the tetrahedral site invalidates the Néel’s two sub-lattice model. We have used the triangular (three sub-lattice) spin arrangement model by Yafet and Kittel (Eq. 5) to calculate the so-called Yafet-Kittel (Y-K) angle (\( \alpha_{Y,K} \)) in order to understand the degree of spin canting and the obtained \( M_s \) values [39]. Furthermore, as the magnetic order of all the spinel ferrites result from the d-electron super-exchange interaction between the tetrahedral (A) and the octahedral (B) sites magnetic ions mediated by the oxygen ions, substituting Sm\(^{3+}\) ions, whose magnetization is due to f-electrons, the existing canted spin arrangement changes and the \( \alpha_{Y,K} \) alters. The calculated values of \( \alpha_{Y,K} \) (Table IV) are ranging between 70-80°. This suggests the existence of canted (triangular) spin arrangement in all the samples (\( y = 0.0-0.05 \)). The values of \( \alpha_{Y,K} \) of the sample with increasing Sm\(^{3+}\) concentration was found to increase. This increase in \( \alpha_{Y,K} \) and the presence of Zn\(^{2+}\) at the tetrahedral (A) site, suggests that there is increasing tendency for triangular spin arrangement on the B-site which results in decreased A-B exchange interaction.

The observation of the increase in magnetization pinning with increase in Sm content agrees with the increase in the area under the hyperfine field distribution (superparamagnetic doublet) as observed by Mössbauer spectroscopy. This effect is pronounced for the sample with \( y = 0.05 \). The increase in coercivity with Sm\(^{3+}\) ion concentration is due to an increased magnetic anisotropy resulting from the pinning of the spins of the Mn\(^{2+}\) and Fe\(^{3+}\) ions at the Sm\(^{3+}\) site. Considering the increase in \( H_c \), the decrease in \( \eta_B \) and decrease in particle size with increase in Sm\(^{3+}\) content suggests that there exists an effective anisotropy due to pinning of the spins which shields the magnetization of the core of the particle from particle-particle interaction which makes the particles more superparamagnetic and the anisotropy appears to be of cubic anisotropy type. Furthermore, as the Mössbauer spectroscopy results depend neither on the particle size nor on the spin glass structure, they suggest the pinning of magnetic moments is due to the magnetic defect created by the presence of Sm\(^{3+}\) ions.

The variations of all the parameters (\( \eta_B, H_c, S \) and \( K \)) with Sm\(^{3+}\) content in the samples extracted from the hysteresis loops can be observed from Table IV. In order to realize the presence of magnetic defects due to Sm-doping, we have calculated the magnetic particle sizes by using Eq. 5. They are listed in Table IV and plotted in Fig. 4.9. To visualize the magnetic pinning induced in the samples due to Sm-doping, we plotted the magnetic...
hyperfine field \( (B_{hf}) \), average crystallite size \( (<d> \) \), magnetic particle size \( (D_m) \) and spectral area under the sextet distribution observed from Mössbauer spectra, against the Sm-content ‘y’ (Fig. 4.8). From the plot, we can observe the decreasing trend of all the parameters with increasing Sm\(^{3+}\) concentration up to \( y = 0.03 \). Interestingly, although crystallite sizes calculated from XRD results decreased continuously with Sm\(^{3+}\) concentration up to \( y = 0.05 \), \( <D_m> \) and Mössbauer spectral area increased while the \( <B_{hf}> \) remains constant for \( y = 0.05 \). This suggests that there are two competing effects present in all our samples: (i) paramagnetism due to lower exchange interaction energy; and (ii) magnetization pinning observed as magnetic (defects) anisotropy and enhanced \( H_c \). The pinning of the spins at higher Sm\(^{3+}\) content is dominant, which increase the magnetic anisotropy as well as \( H_c \). This is also the reason for increase in the area under the superparamagnetic part of the Mössbauer spectra.

### 4.2.5 Mössbauer Spectroscopy analysis

The Mössbauer spectra of all the \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{Sm}_y\text{O}_4 \) samples with \( y = 0, 0.01, 0.03 \) and \( 0.05 \), recorded at RT are shown in Fig. 6. For the samples with \( y = 0.0-0.03 \), a Zeemann split broad (low intensity) sextet and a strong central doublet were seen. With increasing Sm-substitution, the sextet contribution seemed to disappear to an apparent doublet and for the sample with \( y = 0.05 \) only a central doublet was seen. The line width of the central doublet was seen to be high for \( y = 0.05 \). This behaviour was not expected for high Sm-content sample, as the sample may behave like more superparamagnetic. Hence, this change in line width of the central doublet could not be explained only by a distribution of quadrupole doublets. Thus, the spectra corresponding to all samples were initially fit by distributions of sextets and doublets. Due to the limitation in assuming only a certain number of sub-spectra in the NORMOS program, the results showed majorly quadrupole split doublets which overestimate the paramagnetic behaviour for the Sm-substituted samples. Thus, only distributions of sextets were then considered for the least square fit of the observed Mössbauer spectra. However, the results were erroneous, because the isomer shifts corresponding to the sextet distribution and the central doublet are different. Considering the decrease in particle size with Sm content in the samples and that in view of a strong central doublet seen regardless of the composition of the sample with slight increase in width, a distribution of sextets along with a crystalline doublet were then considered as the fitting model for all the samples. During the least square fit to the observed Mössbauer spectra, the
values of $IS, QS$ and line-width of the doublet for all samples were fixed to the approximate values of pure zinc ferrite ($IS = 0.235$ mm/s, $QS = 0.5$ mm/s and line width = 0.45 mm/s) [40, 41]. The spectra after the fit are shown in Fig. 6 and resultant hyperfine parameters are listed in Table III.

From the Mössbauer spectrum of the undoped Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ($y = 0.0$) sample, shown in Fig. 4(a), it is clear that there exists a Zeemann split broad sextet component along with a central doublet. Hence, the spectrum was fit by distribution of sextets and a doublet. We believe that the local compositional fluctuation leads to formation of Zn-ferrite like tiny regions in the sample, which results in the central doublet observed in the Mössbauer spectrum. The origin of the other sub-spectrum (the sextet distributions) could be due to: (i) the slow spin relaxation of the bigger particles from the wide distribution of particle sizes as discussed in section 3.1; and (ii) the partial substitution by Mn$^{2+}$ ions in place of Fe$^{3+}$ ions at the B-site in the spinel structure of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. In the latter case, as observed by XRD results, Zn$^{2+}$ occupies A site and Mn$^{2+}$ is distributed among the available A and B sites, leading to a partial occupation of Fe$^{3+}$ at the A site. The resulting formula can be represented as (Zn$_{0.5}$Mn$_{0.5}$Fe$_3$O$_4$)[Mn$_y$Fe$_{2-y}$O]. Hence, the A-B (Fe$^{3+}$ - Fe$^{3+}$) super-exchange interaction becomes stronger resulting in a broad sextet in the Mössbauer spectrum. The other exchange interaction which might provide magnetic ordering of Fe$^{3+}$ atoms is between Fe$^{3+}$ - Mn$^{2+}$ (A-B interaction). Thus, the magnetic hyperfine field distribution seen in Fig. 4(a) right, is due to the A-B site super-exchange interaction between Fe$^{3+}$ - Fe$^{3+}$ and Fe$^{3+}$-Mn$^{2+}$. We assign the larger $B_{hf}$ ($\sim 35-50$ T) to Fe$^{3+}$ - Fe$^{3+}$ interaction and smaller $B_{hf}$ ($\sim 15-35$ T) to Fe$^{3+}$ - Mn$^{2+}$ interaction. The $B_{hf}$ values in the range 0-10 T, are due to the superparamagnetic relaxation of very small particles present in this sample.

The same fitting model (a sextet distribution and a doublet) was assumed for the least square fitting of all the Sm-doped samples. For these Sm-doped samples, as in the case of undoped Mn-Zn ferrite, the presence of Zn-ferrite-like local tiny regions result in the crystalline central doublet (DX1, where X = 1, 2, 3 and 4, in Table III). During least square fit of the Mössbauer spectra, the values of $IS, QS$ and spectral line widths for this doublet were fixed to 0.235 mm/s, 0.5 mm/s and 0.45 mm/s, respectively, (Table III) [40, 41]. For each sample, the rest of the spectrum was consistently fit by a distribution of sextets as given in Fig. 4.8. From the probability distribution, $P(B_{hf})$, (area under the Zeemann split sextet distribution, Fig. 4.8 and Table III), it can be observed that the average value of $B_{hf}$ ($<B_{hf}>$) decreases with increase in Sm content in the samples. For the sample with $y = 0.01$, the
spectrum fit by distribution of sextets and a single doublet, in a manner similar to that of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (y = 0.0) sample, showed that the intensity of the sextet distribution decreases by Sm-doping.

*Figure 4.8* Least square fit Mössbauer spectra of Mn$_{0.5}$Zn$_{0.5}$Fe$_{2-y}$Sm$_{y}$O$_4$ samples: (a) y = 0.0, (b) y = 0.01, (c) y = 0.03 and (d) y = 0.05, measured at RT. On the right hand side of each spectrum, the distribution profiles of magnetic hyperfine field $P(B_{hf})$ are shown.
The peak values of $P(B_{hf})$ (Table III) are assigned to the magnetic ordering due to Fe$^{3+}$ - Fe$^{3+}$, Fe$^{3+}$ - Mn$^{2+}$ and Fe$^{3+}$ - Sm$^{3+}$ interactions, respectively. The observed value of $<B_{hf}>$ was found to decrease as compared to the undoped sample, which is attributed to the reduced interaction strength due to incorporation of Sm$^{3+}$ as Fe$^{3+}$ - Sm$^{3+}$ interaction is weak. The presence of Sm$^{3+}$ between Fe$^{3+}$ ions also reduces the super-exchange interaction between Fe$^{3+}$ - Fe$^{3+}$.

For the sample with $y = 0.03$, the reduced magnetic ordering (area under the sextet distribution in Fig. 4.8(c)) resulted in further decrease of $<B_{hf}>$ value, due to the increased Fe$^{3+}$ - Sm$^{3+}$ interactions. There were no peaks observed in the $B_{hf}$ distribution corresponding to Fe$^{3+}$ - Fe$^{3+}$ and Fe$^{3+}$ - Mn$^{2+}$ interactions. The sample with $y = 0.05$, showed no clear Zeemann split sextet pattern as the exchange interaction between Fe$^{3+}$ - Sm$^{3+}$ dominated and the observed $B_{hf}$ values were low. Interestingly, for the sample with $y = 0.05$, the $<B_{hf}>$ value is nearly constant to that observed for the sample with $y = 0.03$. This, we believe, is due to the increased pinning of the Fe-moments. This aspect is explained further in section 3.4. For the Sm-substituted samples (with $y = 0.01$ and 0.03), the progressively narrower sextet distributions, which appear as doublets in the Mössbauer spectra, signify the superparamagnetic nature of small particles in the samples. The samples with $y = 0.05$ showed only superparamagnetic contribution due to very small crystallites (~ 3-13 nm) which is confirmed by XRD and TEM results (Table I). Surprisingly, the width of the sextet distribution which appears as a doublet was found to increase for sample $y = 0.05$ in comparison to the sample with $y = 0.03$. Simultaneously, the rate of decrease of the spectral area under the doublet considerably reduced (Table III). The origin of this behavior is explained as follows. It is well known that introduction of Sm$^{3+}$ results in hard magnetic property [42], although there are reports on reduced magnetic anisotropy. The magnetic anisotropy enhancement/reduction due to Sm$^{3+}$ doping depends on the type and position of other cations in the lattice. For all the samples, we have observed the enhancement of magnetic anisotropy [11] with increasing Sm$^{3+}$ concentration in vibrating sample magnetometry studies. Thus, we attribute the broadening of the central doublet with Sm concentration to the enhancement of hard magnetic behaviour due to the pinning of magnetic moments in the sample which appears as a re-entrant magnetic ordering.

To emphasize, a superparamagnetic doublet was observed in addition to a (fixed width) crystalline quadrupole doublet in the Mössbauer spectra of all samples (Table III). The average magnetic hyperfine field $<B_{hf}>$ was seen to decrease with increasing Sm-content, suggesting the increase in superparamagnetic behaviour of the nanoparticles. However, for
the sample with \( y = 0.03 \) and 0.05, the nearly constant \( \langle B_{hf} \rangle \) (Table III) is due to the enhancement in the pinning of the Fe-spins at the ‘defect’ created in the bulk of the nanoparticles in the sample with \( y = 0.05 \). The crystalline doublet is assigned to the paramagnetic property of zinc ferrite (ZnFe\(_2\)O\(_4\)) type-local atomic ordering in the samples. The compositional disorder in the samples might have been produced due to local disorder in the arrangement of Mn\(^{2+}\), Zn\(^{2+}\) and Fe\(^{3+}\) ions in the available tetrahedral and octahedral sites.

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**Figure 4.9:** Variation of selected structural and magnetic parameters of the Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_{2-y}\)Sm\(_y\)O\(_4\) samples with ‘y’. In the plot, the variation in magnetic hyperfine field (\( B_{hf} \)), average crystallite size (\( <d> \)), magnetic particle size (\( D_m \)) and crystalline spectral area show a similar trend with the Sm-content ‘y’. The Y-scale in the plot corresponds to the actual measured value of \( B_{hf} \), whereas the Y-scales corresponding to \( D_m \) values (in nm) are enhanced by a factor of 3, \( <d> \) values (in nm) are enhanced by a factor of 1.5 and the spectral area values (in %) are reduced by a factor of 3 for the purpose of comparison in the same plot.
Table III. Mössbauer spectral parameters obtained after the least square fitting of the Mössbauer spectra (Fig. 4.9) of Mn$_{0.5}$Zn$_{0.5}$Fe$_{2-y}$Sm$_{y}$O$_4$ samples. Average values of isomer shift ($<\text{IS}>$) and magnetic hyperfine field ($<\text{B}_\text{hf}>$), quadrupole splitting ($Q\text{S}$), relative spectral area and spectral line width (FWHM) are listed. Sub-spectra designated by S and D abbreviate for sextet distributions and doublet, respectively. The values of IS are given with respect to the $^{57}\text{Co}$-source (Rh-matrix).

<table>
<thead>
<tr>
<th>$y$ (mole fraction)</th>
<th>Sub-spectrum</th>
<th>$&lt;\text{IS}&gt;$ (mm/s)</th>
<th>$Q\text{S}$ (mm/s)</th>
<th>$&lt;\text{B}_\text{hf}&gt;$ (T) (± 0.5 T)</th>
<th>Peak values at $P(B_{\text{hf}})$</th>
<th>Spectral area (%)</th>
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<tbody>
<tr>
<td>0.00</td>
<td>S11</td>
<td>0.204</td>
<td>-0.023</td>
<td>24.34</td>
<td>3.6, 9, 25, 46</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>D11</td>
<td>0.235</td>
<td>0.500</td>
<td></td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>0.01</td>
<td>S21</td>
<td>0.195</td>
<td>0.008</td>
<td>13</td>
<td>4.5, 17, 37</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>D21</td>
<td>0.235</td>
<td>0.500</td>
<td></td>
<td></td>
<td>47</td>
</tr>
<tr>
<td>0.03</td>
<td>D31</td>
<td>0.226</td>
<td>-0.039</td>
<td>8.1</td>
<td>4.5</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>D32</td>
<td>0.235</td>
<td>0.500</td>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>0.05</td>
<td>D41</td>
<td>0.187</td>
<td>-0.064</td>
<td>7</td>
<td>4.5</td>
<td>64</td>
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<tr>
<td></td>
<td>D42</td>
<td>0.235</td>
<td>0.500</td>
<td></td>
<td></td>
<td>36</td>
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Table IV. The magnetic parameters obtained from the M-H loops for Mn$_{0.5}$Zn$_{0.5}$Fe$_{2-y}$Sm$_{y}$O$_4$ samples. Saturation magnetization ($M_s$), remanence ($M_r$), reduced remanence $S (= M_r/M_s)$, coercivity ($H_c$), magneton number ($\eta_B$), anisotropy constant ($K$), Y-K angle ($\alpha_{Y,K}$), initial susceptibility ($\chi_i$) and upper limit of the magnetic particle size ($D_m$) for the samples are listed against Sm$^{3+}$ concentration ($y$).

<table>
<thead>
<tr>
<th>$y$ (mole fraction)</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r$ (emu/g)</th>
<th>$S$</th>
<th>$H_c$ (Oe)</th>
<th>$K$ (erg/Oe)</th>
<th>$\eta_B$ (\mu$_B$)</th>
<th>$\alpha_{Y,K}$ (°)</th>
<th>$\chi_i$</th>
<th>$D_m$ (nm)</th>
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<tbody>
<tr>
<td>0.00</td>
<td>24.6</td>
<td>3.01</td>
<td>0.122</td>
<td>68</td>
<td>1698</td>
<td>1.0387</td>
<td>76.61</td>
<td>0.07</td>
<td>7.9</td>
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<tr>
<td>0.01</td>
<td>20.7</td>
<td>0.66</td>
<td>0.033</td>
<td>21</td>
<td>441</td>
<td>0.8775</td>
<td>77.38</td>
<td>0.0404</td>
<td>7.5</td>
</tr>
<tr>
<td>0.03</td>
<td>12.4</td>
<td>8.09</td>
<td>0.655</td>
<td>1258</td>
<td>24275</td>
<td>0.5277</td>
<td>79.21</td>
<td>0.0017</td>
<td>3.6</td>
</tr>
<tr>
<td>0.05</td>
<td>4.8</td>
<td>3.26</td>
<td>0.676</td>
<td>1453</td>
<td>10947</td>
<td>0.2076</td>
<td>81.04</td>
<td>8.9E-4</td>
<td>5.4</td>
</tr>
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</table>
4.3 Summary

Samarium substituted Mn-Zn ferrites were successfully synthesized by solution combustion route using a mixture of fuels (urea and glucose). The effect of Sm³⁺ ion substitution on the structural and magnetic properties of these ferrites was studied at room temperature. The X-ray diffraction revealed that all the samples were mono-phased with cubic spinel structure. The crystallites were in nano-size regime. The average crystallite size decreased with increasing Sm concentration. The position of absorption bands in FTIR spectra confirmed the formation of cubic spinel ferrite. The Sm-substituted Mn-Zn ferrite particles showed enhanced hard ferrimagnetic nature with increasing Sm-content. The value of saturation magnetization was found to decrease, but, the coercivity increased with Sm-content. Also, the magnetic particle size and magneton number were found to decrease gradually with the increase in Sm³⁺ concentration. The paramagnetic-like Sm³⁺ ion substitution in octahedral site reduced the exchange interaction between A and B sites that resulted in decrease of saturation magnetization. Furthermore, Mössbauer spectroscopy results suggest the existence of local disorder in the arrangement of cations in the sub-lattice of samples. Also, the pinning of magnetic moments was found to be solely due to Sm³⁺ ions with related effects arising from particle size variation. These observations in our sample suggest that the synthesized ferrites can be potentially used in applications involving a wide range of frequencies.
4.4 References


[31] O. M. Hemeda, IR spectral studies of Co<sub>0.6</sub>Zn<sub>0.4</sub>Mn<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub> ferrites, J. Magn. Magn. Mater. 281 (2004) 36-41.


CHAPTER-4

PART-B

Gamma irradiation effect on Mn$_{0.5}$Zn$_{0.5}$Sm$_y$Fe$_{2-y}$O$_4$

In this Part, we report the modification in the structural and magnetic properties of Sm$^{3+}$ substituted Mn-Zn ferrite irradiated by different doses (0, 15 and 25 kGy) of high energy gamma irradiation.
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PART-B

4.5 Motivation

The recent developments in measuring devices and data acquisition modules in nuclear reactors and accelerators raise the problem in the irradiation effects on electronic components. Even the satellites and spacecraft’s can be exposed to cosmic radiation of high dose. The radiation may cause excitation, ionization of atoms in the structure of matter [1]. Gamma rays may be produce defects in the materials by affecting the structural, morphological, electrical and magnetic properties of nano ferrites. The properties of nano-size ferrites depend on synthesis techniques and chemical composition [2, 3]. The interaction of radiant energy, especially γ-radiation, with matter is an important area of research in healthcare [4], industry [5] and related materials from the applications point of view [6-8]. Controlled irradiation of gamma rays can produce tunable amount of crystallographic defects in materials. The change in structural properties of ferrite systems by gamma irradiation is an important area of research. Hence, a lot of attention is devoted towards the study of γ-irradiation induced defect creation and modification in the physical properties of nano-size ferrite materials with different doses and dose rates [10-13]. The change in the structural and magnetic properties of ferrites when irradiated by gamma rays, it has been reported earlier [14] that it may be due to the breaking of ferrimagnetic ordering, surface state pinning, cation inversion, etc. Hence, in this work, we report the modification in the structural and magnetic properties of Sm\(^{3+}\) substituted Mn-Zn ferrite irradiated by different doses (0, 15 and 25 kGy) of high energy gamma irradiation.

4.6 Results

Fig. 1 shows the Rietveld refined XRD patterns of the Mn\(_{0.5}\)Zn\(_{0.5}\)Sm\(_{x}\)Fe\(_{2-x}\)O\(_4\) pristine samples and the samples after γ-irradiation (15 kGy and 25 kGy). Comparing the XRD patterns of all the pristine samples (Fig. 1 (a, d, g)) it is clear that the FWHM of the XRD peaks increased with increase in Sm\(^{3+}\) content in the samples, i.e., the crystallite size decreases, as observed earlier [15]. The mass density also increases as heavier rare earth (Sm) atoms are added (Table 1). After 15 and 25 kGy of γ-irradiation the crystalline structure of the samples remains intact (Fd-3m), but the feature of the XRD peaks were changed. After 15 kGy of γ-irradiation the base of the XRD peaks becomes broad (Fig. 1 (b, c, h)) indicating
that the average crystallite size decreases but the strain in the lattice increases. Hence, the $\gamma$-radiation creates disorder in the spinel lattice of the samples. The Rietveld refined lattice

![Rietveld refined XRD patterns](image)

Figure 1: The Rietveld refined XRD patterns of the Mn$_{0.5}$Zn$_{0.5}$Sm$_x$Fe$_{2.8}$O$_4$ pristine samples with $x = 0.01$ (a), 0.03 (d), and 0.05 (f). The respective sample after 15 kGy (b, d, h) and 25 kGy (c, f, i) $\gamma$-irradiation are also shown. The indexed Bragg positions in (a) correspond to the cubic spinel phase. The same indices are valid for all other XRD patterns shown. The arrow mark (\(\downarrow\)) in (i) represents the position of the MnO$_2$ (Pnam) (110) reflection. Cu-K$_\alpha$ radiation ($\lambda = 1.54 \, \text{Å}$).

parameters are given in Table 1. The lattice parameters were found to decrease after $\gamma$-irradiation, which was also observed earlier with low doses of $\gamma$-irradiation in pure (without Sm doping) Mn-Zn ferrite powders [18,19]. The shape of the XRD peaks indicates a distribution of particle sizes. A reasonably good fit to the peaks could not be obtained using only a single Voigt profile. In order to quantify the particle sizes, we have fit the (311) XRD peaks with two Gaussians (Fig. 2). The FWHM of the sharp peak provides the maximum average crystallite size and that of the broad peak provides the minimum average crystallite size. The obtained crystallite sizes using Scherrer formula: $D = \frac{K\lambda}{\beta\cos\theta}$, where $D$ is the
crystallite size, $K$ is the shape factor, $\beta$ is the FWHM of the peak at angle 20 and 0 is the Bragg angle [20], are listed in Table 1.

It is now well established that after high dose (50 kGy) of $\gamma$-irradiation $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ phase transforms mostly into crystalline $\text{ZnFe}_2\text{O}_4$ and $\alpha$-$\text{Fe}_2\text{O}_3$ along with amorphous MnO phase [21]. In the presence of rare earth elements such as Sm and Gd, the transformation is modified [22]. Hence, the content of Sm and Gd controls the phase transformation process and the resultant compound formation.

Figure 2: The Gaussian fit to the (311) XRD peak of the respective samples as given in Fig. 1. The (311) peak in every figure is fit with two Gaussians as seen. The low intensity (222) peak is also considered in the fitting.

After 15 kGy of $\gamma$-irradiation of the sample S1, the FWHM of the (311) peak (Fig. 2) becomes larger. The crystallite size and the lattice parameter both decrease in comparison to that of the pristine sample (Table 1). Hence, a low dose of (15 kGy) $\gamma$-irradiation creates disorder in the spinel ferrites. However, after 25 kGy $\gamma$-irradiation (sample S1-25) the crystallite size and the lattice parameter, both increased in comparison to that of the sample irradiated with a $\gamma$-dose of 15 kGy (S1-15). But, the lattice parameter value is still below that of the pristine sample (S1). This observation indicates that, by increasing the $\gamma$-dose from 15
kGy to 25 kGy the sample becomes more crystalline and there may be a tendency of local phase transformation from one phase with lower lattice parameter to another with higher

Table 1. The structural parameters obtained by Rietveld refinement of the XRD patterns of the \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Sm}_{x}\text{Fe}_{2-x}\text{O}_4 \) samples irradiated with different dosed of \( \gamma \)-irradiations. \( L \) represents the crystallite size obtained by Scherrer formula using the (311) peak in Fig. 2. The \( L_{\text{av}} \) is the average crystallite size obtained using the FWHM obtained from the Rietveld refinement of the XRD patterns. \( L_{\text{max}} \) and \( L_{\text{min}} \) are respectively the maximum and minimum crystallite sizes obtained using the sharp and broad Gaussian in Fig. 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>V (Å³)</th>
<th>ρ (g/cc)</th>
<th>( L ) (crystallite size, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( L_{\text{av}} )</td>
</tr>
<tr>
<td>S1</td>
<td>8.4293</td>
<td>598.9</td>
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</tr>
<tr>
<td>S3</td>
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<td>596.5</td>
<td></td>
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<td>S5-25</td>
<td>8.4253</td>
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<td>8.8</td>
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</table>

lattice parameter. It can be envisaged by considering earlier literature \([21, 22]\) that a higher \( \gamma \)-dose of 50 kGy transforms the similar, \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_{2}\text{O}_4 \) material mostly to crystalline \( \text{ZnFe}_2\text{O}_4 \) phase along with \( \alpha\text{-Fe}_2\text{O}_3 \) phase (and amorphous \( \text{MnO} \) phase) \([21]\), however, \( \text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2-0.06}\text{Gd}_{0.03}\text{Sm}_{0.03}\text{O}_4 \) phase transforms mostly into crystalline \( \text{ZnFe}_2\text{O}_4 \) phase, along with crystalline \( \alpha\text{-Fe}_2\text{O}_3 \) phase and small quantity of \( \text{MnO}_2 \) phase \([22]\). In both the cases \( \text{ZnFe}_2\text{O}_4 \) is the major phase observed after 50 kGy dose of \( \gamma \)-irradiation. As the present sample is similar to the above samples, we do expect that the present sample should also transform similarly with \( \text{ZnFe}_2\text{O}_4 \) as the major product phase. An irradiation dose of 25 kGy might initiate the formation of \( \text{ZnFe}_2\text{O}_4 \) phase. To strengthen our assumption further, it is worth noting that we do not observe any major change in the position of the XRD peaks as the structure of \( \text{ZnFe}_2\text{O}_4 \) is also spinel. Again, the lattice parameter of pure \( \text{ZnFe}_2\text{O}_4 \) is higher than any of the \( \text{Mn-Zn} \) ferrite spinel phase. So, it is notionally correct that the observed lattice parameter for the sample irradiated with 25 kGy is higher from that of the sample irradiated with a dose of 15 kGy. Hence, the sample S1-25 is the transient state before formation of \( \text{ZnFe}_2\text{O}_4 \) phase.
Under different doses of $\gamma$-irradiation, we have observed similar behavior for the lattice parameter of the sample S3 (Fig. 2 (d, e, f)) as that of the sample S1, except that the crystallite size decreases (FWHM increases) continuously as the $\gamma$-irradiation dose increases. The high dose $\gamma$-irradiation study of similar material, namely, $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2.04}\text{Gd}_{0.02}\text{Sm}_{0.02}\text{O}_4$ and $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2.02}\text{Gd}_{0.01}\text{Sm}_{0.01}\text{O}_4$ samples, both transform to $\text{ZnFe}_2\text{O}_4$ (along with $\alpha\text{-Fe}_2\text{O}_3$) after 50 kGy of $\gamma$-irradiation, however, the later compound ($\text{ZnFe}_2\text{O}_4$) shows broader XRD lines (more disorder and smaller particle size [22]). Hence, for our present sample S3 after $\gamma$-irradiation we should expect broad lines in comparison to S1. Hence, the observed decrease in crystallite size with increasing $\gamma$-irradiation dose in sample S3 is rational.

The XRD pattern of the sample S5 after $\gamma$-irradiation showed a different behavior than that of the other two studied samples (S1 and S3) (Fig. 2). But, the present material (sample S5) is similar to the $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2.06}\text{Gd}_{0.03}\text{Sm}_{0.03}\text{O}_4$ sample (with rare earth substitution of x = 0.06). In this material, S5, formation of crystalline $\text{MnO}_2$ ($\text{Pn}\text{m}$) as major product phase and $\text{ZnFe}_2\text{O}_4$ as minor phase, was observed after 50 kGy of $\gamma$-irradiation [22]. Hence, we expect the phase transformation in S5 to proceed with the tendency to form $\text{MnO}_2$, unlike in the case of S1 and S3 where is the major expected phase is $\text{ZnFe}_2\text{O}_4$ after 50 kGy of $\gamma$-irradiation. We may consider that when the the rare earth (Sm) atoms leave the spinel lattice giving rise to the relatively sharper peak for the stress-relaxed $\text{ZnFe}_2\text{O}_4$ phase. For higher dose (25 kGy) of $\gamma$-irradiation (sample S5-25) the formation of $\text{MnO}_2$ phase dominates and the (311) peak becomes broad before diminishing to the extent of the contribution from a small amount of $\text{ZnFe}_2\text{O}_4$ phase as observed earlier [22]. However, the sharper peak for the S5-15 sample (Fig. 2(h)) in comparison to that of S5 and S5-25 sample (Fig. 2(g) and (i), respectively) suggests that the $\text{MnO}_2$ formation (as observed after 50 kGy $\gamma$-irradiation [22]) proceeds through the formation of amorphous $\text{MnO}_2$ phase after 25 kGy of $\gamma$-irradiation.

In order to understand the observed reduction of the lattice parameter with $\gamma$-irradiation dose, we have analyzed the occupancy of the Sm and Mn atoms through the Fullprof software. We observed that the vacancies of the Sm and Mn-sites in the spinel structure leads to decrease of the lattice parameter and the unit cell volume. Hence, we conclude that the Sm atoms are initially (and then Mn atoms at higher doses) came out of the tetrahedral/octahedral sites in the unit cells where these atoms were occupied, before the spinel unit cell is damaged and the other phases, like $\text{MnO}_2$ and $\text{ZnFe}_2\text{O}_4$ etc., were formed at higher $\gamma$-irradiation doses.
as observed earlier [21,23,24].

Effective pinning of the Fe spins at the Sm sites (which acts as a paramagnetic defect centre in the Mn-Zn ferrite crystal) introduces magneto-crystalline anisotropy in these materials [15]. Hence, the coercivity of the virgin materials increases with increasing Sm content (Fig. 3). However, the low magnetic interaction and ordering of the Sm atoms with Fe/Mn atoms reduces the saturation magnetization with increasing Sm doping. Hence, with increasing ‘x’ in Mn$_{0.5}$Zn$_{0.5}$Sm$_{x}$Fe$_{2-x}$O$_4$ (pristine) samples the saturation magnetization is decreasing, but the coercivity is increasing.

After $\gamma$-irradiation we have observed a small variation in the saturation magnetization values of the samples (Fig. 3). In sample S1, the $M_s$ value (18.7 emu/g) decreases after 15 kGy of $\gamma$-irradiation, while it increases after 25 kGy of $\gamma$-irradiation. For the S1-15 sample, it seems that the disorder (observed as increased FWHM of the XRD peaks, decreased particle size) caused due to $\gamma$-irradiation reduces the saturation magnetization in the sample to 14.1 emu/g. Furthermore, after 25 kGy of $\gamma$-irradiation dose (sample S1-25), the cation disorder (i.e., Zn atoms at the octahedral site at this transient state of phase transformation to ZnFe$_2$O$_4$) might be the reason for the higher saturation magnetization (20.3 emu/g). All the samples (S1, S1-15 and S1-25) behave superparamagnetically.

For the S3, S3-15 and S3-25 samples the disorder increases with the $\gamma$-irradiation dose, as observed via the increase in the FWHM of the XRD peaks (Fig. 2(d, e, f)). This increase in disorder might also be leading to the observed decrease of saturation magnetization (Table 2). Interestingly, after $\gamma$-irradiation the coercivity of the sample S3 reduces to about zero (Fig. 3(b)). This suggests that $\gamma$-irradiation can be used to tune the coercivity (magnetic hardness) of the materials. Moreover, it seems that the Sm atoms do not play any role in providing magnetic anisotropy (and coercivity) after $\gamma$-irradiation (the S3-15 and S3-25 samples). This observation suggests that Sm atoms are firstly coming out of the spinel lattice of the samples making the material soft ferromagnetic even at this low dose of 15 kGy.

The sample S5, which shows further low saturation magnetization but higher coercivity, but it reduces its coercivity to zero after $\gamma$-irradiation (Fig. 3(c)). This also suggests that 15 kGy of $\gamma$-irradiation is high enough for the Sm (bigger rare earth) atoms to come out of the spinel lattice confirming their highly metastable nature. Interestingly, for these samples (after $\gamma$-irradiation, S5-15 and S5-25), like the other samples, the variation of the saturation magnetization scales with disorder of the spinel (Mn-Zn ferrite) phase.
Figure 3: The M-H loops of Mn$_{0.5}$Zn$_{0.5}$Sm$_x$Fe$_{2-x}$O$_4$ samples before and after different doses of γ-irradiations.

Table 2. The saturation magnetization and the coercivity obtained from the magnetometry results for the studied Mn$_{0.5}$Zn$_{0.5}$Sm$_x$Fe$_{2-x}$O$_4$ samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_s$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>18.7</td>
<td>20</td>
</tr>
<tr>
<td>S1-15</td>
<td>14.1</td>
<td></td>
</tr>
<tr>
<td>S1-25</td>
<td>20.4</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>10.4</td>
<td>1265</td>
</tr>
<tr>
<td>S3-15</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td>S3-25</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>4.3</td>
<td>1420</td>
</tr>
<tr>
<td>S5-15</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>S5-25</td>
<td>6.2</td>
<td></td>
</tr>
</tbody>
</table>

The Mössbauer spectra of all the studied samples are shown in Fig. 4. All the samples give rise to similar spectra consisting of a broad doublet. The presence paramagnetic defects, like Sm atoms, and the non-magnetic Zn-atoms in the Mn$_{0.5}$Zn$_{0.5}$Fe$_{2-x}$Sm$_x$O$_4$ samples is responsible the low hyperfine field of the Mössbauer spectra [15]. All the spectra were fit using a crystalline doublet and a broad sextet distribution. The Mössbauer spectral parameters obtained from the fitting are given in Table 2. Considering the isomer shift (IS ≈ 0.24 mm/s) and the quadrupole splitting (QS ≈ 0.50 mm/s) values of all the studied samples, the central crystalline doublet in all the respective spectrum is assigned to the ZnFe$_2$O$_4$ type of local regions in the sample [25, 26], which is paramagnetic in nature. After gamma irradiation the corresponding area of this doublet decreases suggesting that there is a tendency for the formation (precipitation) of ZnFe$_2$O$_4$ phase in all the samples, which maybe is a more stable phase than Mn-Zn ferrite under γ-irradiation. The hyperfine field distribution P(B$_{hf}$) of the sample S1 shows the dominant peak at B$_{hf}$ = 4.5 T and few small intensity peaks at higher B$_{hf}$.
values (Fig. 4(a), right). The higher $B_{hf}$ peaks are absent in sample S3 and S5. This proves the

Figure 4: The Mössbauer spectra of the $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Sm}_{0.5}\text{Fe}_{2.5}\text{O}_4$ samples before and after different doses of $\gamma$-irradiations.

Table 3. Mössbauer spectral parameters for all the analyzed $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Sm}_{0.5}\text{Fe}_{2.5}\text{O}_4$ samples. Subspectra designated by S and D abbreviate for the corresponding sextet distributions and doublet, respectively, in Fig. 5. The values of isomer shift (IS), quadrupole splitting (QS), average magnetic hyperfine field ($<B_{hf}>$) and relative spectral area are listed. The parameters (IS, $2\varepsilon$ and $<B_{hf}>$ values given for the sextet are the averaged quantities. The magnetic hyperfine field ($B_{hf}$) is the peak value in the distribution $(P(B_{hf}))$. The isomer shift values are given relative to $^{57}\text{Co}$ source (Rh matrix) at RT (which produces a value of -0.106 mm/s in $\alpha$-Fe foil at RT).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sub-spectrum</th>
<th>IS (mm/s)</th>
<th>$2\varepsilon$ or QS (mm/s)</th>
<th>$B_{hf}$ (&lt; $B_{hf}$&gt; (T)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>S</td>
<td>0.23</td>
<td>0.01</td>
<td>4.5 (13.02)</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.23</td>
<td>0.50</td>
<td></td>
<td>47</td>
</tr>
<tr>
<td>IS1-15</td>
<td>S</td>
<td>0.19</td>
<td>0.00</td>
<td>4.5 (17.21)</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.25</td>
<td>0.47</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>IS1-25</td>
<td>S</td>
<td>0.23</td>
<td>0.04</td>
<td>4.5 (13.47)</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.24</td>
<td>0.46</td>
<td></td>
<td>51</td>
</tr>
<tr>
<td>S3</td>
<td>S</td>
<td>0.26</td>
<td>0.04</td>
<td>4.5 (8.11)</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.23</td>
<td>0.50</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>IS3-15</td>
<td>S</td>
<td>0.36</td>
<td>0.27</td>
<td>4.5 (7.22)</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.24</td>
<td>0.49</td>
<td></td>
<td>49</td>
</tr>
<tr>
<td>IS3-25</td>
<td>S</td>
<td>0.25</td>
<td>0.13</td>
<td>4.5 (7.81)</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.25</td>
<td>0.48</td>
<td></td>
<td>54</td>
</tr>
<tr>
<td>S5</td>
<td>S</td>
<td>0.20</td>
<td>-0.06</td>
<td>4.5 (7.00)</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.23</td>
<td>0.50</td>
<td></td>
<td>36</td>
</tr>
<tr>
<td>IS5-15</td>
<td>S</td>
<td>0.20</td>
<td>-0.05</td>
<td>4.5 (6.76)</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.24</td>
<td>0.51</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>IS5-25</td>
<td>S</td>
<td>0.20</td>
<td>-0.06</td>
<td>4.5 (6.73)</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.24</td>
<td>0.48</td>
<td></td>
<td>33</td>
</tr>
</tbody>
</table>
weak magnetic ordering in S3 and S5 samples than S1 sample. This supports the decrease in saturation magnetization with increasing Sm content in the samples, as observed in Fig. 3.

After γ-irradiation of sample S1, the sample S1-15, shows a bit better magnetic ordering as the higher $B_{hf}$ peaks in P($B_{hf}$) (Fig. 4(b), right) are more intense than that for sample S1. However, in sample S1-25, the intensity of the higher $B_{hf}$ peaks decreases. This observation is in line with the XRD results that S1-15 sample is more disordered (higher FWHM) compared to that of the S1 sample. However, the higher saturation magnetization for S1-25 sample (Fig. 3(a)) might be due to a partial Zn$^{2+}$ cation occupation at the octahedral site, which is not observed in the Mössbauer spectrum in Fig. 4(c). For samples S3, S3-15 and S3-25, there is a monotonous decrease of the superparamagnetic contribution (area of the sextet distribution) in the Mössbauer spectrum. This agrees well with the decrease in coercivity and saturation magnetization (Fig. 3(b)) with increasing doses of the γ-irradiation. The superparamagnetic nature of the sample can also be inferred from the fact that the FWHM of the XRD peaks were found to increase with increasing dose of γ-irradiation (Fig. 2(d, e, f)). The coercivity of the sample S5 reduce to zero after γ-irradiation, but the saturation magnetization of S5-15 is a bit lower and that of S5-25 is a bit higher, as discussed above. The area (Table 2) under the superparamagnetic contribution sextet distribution in Fig 4 (g, h, i) varies similarly. This observed variation can be rationalized with the observed trend in the variation of the FWHM of the disordered (XRD) peaks in Fig. 2 (g, h, i) and the saturation magnetization (Fig. 3 (c)).

The FTIR spectra of all the studied samples are shown in Fig. 5. The two absorption bands corresponding to the vibrations of the tetrahedral ($v_1 \sim 540-580$ cm$^{-1}$) and octahedral

![Figure 5: The FTIR spectra of the Mn$_{0.5}$Zn$_{0.5}$Sm$_{0.5}$Fe$_2$O$_4$ samples, before and after different doses of γ-irradiations. The spectra are shifted vertically for clarity.](image-url)
(ν₂ ~ 350-400 cm⁻¹) site cations were observed [15]. This confirms the retention of the spinel ferrite phase of the samples even after 25 kGy of γ-irradiation, which agrees well with the XRD results. However, the octahedral band of the γ-irradiated samples appear weak in comparison to that of the pristine samples. This indicates that γ-irradiation favors the removal of octahedral site ions (mainly Sm and partially Mn) and indicates the presence / formation of ZnFe₂O₄ phase.

4.7 Summary

The pellets of Sm doped Mn₀.₄Zn₀.₆Zn₀.₆Fe₂O₄ samples were exposed to high energy γ-irradiation of different doses (0, 15 and 25 kGy). The change in structure and magnetic properties of these samples were studied in detail and compared with earlier results. We conclude that up to 25 kGy of γ-irradiation the studied samples retain their spinel structure as observed by XRD. However, the observed lattice parameter after γ-irradiation are less than that observed for the pristine samples. This decrease in lattice parameter might be due to the shrinkage of the unit cell after removal of Sm and Mn atoms from their respective lattice sites by the γ-irradiation. The γ-irradiation creates defects/vacancies in the spinel structure which was observed as broadening of the FWHM of the XRD peaks and reduction in FTIR absorption intensity of the octahedral band. The exhibition of the superparamagnetic behavior, transformation of the material from relatively hard magnetic nature to soft magnetic nature and reduction in area of the magnetic hyperfine field in the Mössbauer spectra are the consequence of the γ-irradiation induced defect/vacancy creation. The structural and magnetic property transformations at low doses of γ-irradiation are envisaged as an intermediate state of the transformation of the samples, which generally transforms to crystalline ZnFe₂O₄, MnO₂ and α-Fe₂O₃ phases at higher doses (~ 50 kGy) of γ-irradiation. Our results help in understanding the structural stability (degradation behavior) of the ferrite materials and the performance of the magnetic devices used near intense radiation sources such as synchrotron and free electron laser facilities.
4.8 References:


[23] J. V. Angadi, A.V. Anupama, R. Kumar, H.M. Somashekarappa, S. Matteppanavar, B. Rudrashwamy, B. Sahoo, Dose dependent modifications in structural and magnetic properties of gamma-irradiated nanocrystalline Mn0.5Zn0.5Fe2O4 ceramics, Ceramics International (submitted) 2016.


CHAPTER-4

PART-C

Effect of Sm$^{3+}$ substitution and magnetic investigation of nano sized Mn$_{0.4}$Zn$_{0.6}$Sm$_{y}$Fe$_{2-y}$O$_{4}$

In this section, we considered previous samples with different optimised compound i.e Mn$_{0.4}$Zn$_{0.6}$Sm$_{y}$Fe$_{2-y}$O$_{4}$ were prepared by solution combustion method to achieve the low cohercivity. We report on the studies of room temperature (RT) crystal structure, vibrational sample magnetometry study and mozzarella spectroscopic study of Mn$_{0.4}$Zn$_{0.6}$Sm$_{y}$Fe$_{2-y}$O$_{4}$ (y = 0.0, 0.02, 0.03, 0.04 and 0.05. It is found that on increasing Sm$^{3+}$ concentration, XRD analysis reveals that all the prepared samples exhibit single phase cubic spinel without any secondary phase. The absorption bands in FTIR are found in the expected range of spinel ferrites. TEM images show the samples are spherical in shape and agglomerated. The magnetic behavior of pure and samarium doped manganite ferrite particles shows soft ferrimagnetic nature. The decrease in saturation magnetization and remnant magnetization is attributed to the weak magnetic interaction.
4.9 Motivation

The rare earth substituted ferrites are nowadays under extensive investigations and are becoming promising materials for various applications. Studies on rare earth ferrites have shown that they are more effective for the relief of acute and chronic pain or discomfort due to the various injuries and ailments. It is well known that the rare earth ions have unpaired 4f electrons screened by 5s and 5p orbital and are almost not affected by the potential field of surroundings ions. The substitution of rare earth ions in to spinel ferrites results in occurring of 4f-3d couplings which determine the magneto crystalline anisotropy in ferrites and can also improve the electrical and magnetic properties of spinel ferrites. By Substitutiong Sm$^{3+}$ at iron site will tune the structural and magnetic properties at room temperature. The composition dependent cubic structural and magnetic properties will be understood and improve the magnetic properties at RT.

4.10 Results

4.10.1 Structural analysis by XRD

Figure 1. shows the rietveld refinement of XRD pattern of as-prepared Mn$_{0.5}$Zn$_{0.5}$Sm$_x$Fe$_{2-x}$O$_4$ (x =0.00, 0.01, 0.03 and 0.05) nanostructured particles from which proper phase identification cannot be observed. Analysis of XRD pattern confirms the presence of strong diffraction peaks corresponding to the planes (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1/3 3 3), (4 4 0), indicating the formation of spinel cubic structure. After certain limit, Sm accumulates at the grain boundaries of Mn-Zn Ferrite and forms orthorhombic phase. This may be due to the presence of SmFe$_2$O$_3$ phase formed due to high reactivity of iron with samarium. The lattice constant (Table 1) is found to increase with increase in Sm$^{3+}$ ion concentration which is attributed to the fact that the ionic radii of Fe$^{3+}$(0.67Å) is smaller than that of Sm$^{3+}$(0.99Å) ions substituted for Sm$^{3+}$ ions. This confirms the occupancy of samarium on octahedral site [26]. The particles size of the powder samples estimated from the full width at half maxima of pattern (FWHM) of their (311) XRD planes by employing Debye- Scherrer relation [1-4]. The average particle size of the samples is in the range of 10-27 nm.
Figure 1: As synthesized retvield refinement X-ray powder diffraction for Mn$_{0.9}$Zn$_{0.1}$Sm$_x$Fe$_{2.8}$O$_4$ ($x = 0.00, 0.01, 0.02, 0.03, 0.04$ and $0.05$)

4.10.2. FTIR analysis

The infrared spectrum is an important tool to probe various ordering phenomenon, and this technique provides the information about position of ions in the crystal and also about the crystal vibrational modes [1]. Infrared spectra of the samples with composition $x = 0.01, 0.03, 0.05$ are shown in Figure 2. Infrared spectra of all the samples have shown two prominent absorption bands, $v_1$ near 600 cm$^{-1}$ attributed to tetrahedral complexes and $v_2$ around 400 cm$^{-1}$ assigned to octahedral complexes. The position of the absorption bands listed in Table 1. The difference in frequencies between $v_1$ and $v_2$ is due to changes in bond
length (Fe\(^{3+}\)-O\(^{2-}\)) at tetrahedral and octahedral sites [2]. The slight change in band position, particularly in \(v_1\) and \(v_2\) suggests the method of preparation, grain size and porosity can influence in locating the band position [3]. It can be seen that the absorption band \(v_1\) not shown any splitting or shoulders and hence the possibility of Fe\(^{2+}\) ions at A-sites is ruled out [4]. On substitution of Sm\(^{3+}\) ion content, \(v_1\) continued to be widen is attributed to atomic mass and volume of the dopant, which affect Fe-O distances on octahedral sites, suggesting that Sm\(^{3+}\) ions occupied octahedral lattice sites [5]. The shift occur in absorption bands \(v_1\) and \(v_2\) for each octahedral and tetrahedral site due to the perturbation occurring in the Fe\(^{3+}\)-O\(^{2-}\) bond by introducing Sm\(^{3+}\) ions [5].

![FTIR spectra](image)

*Figure 2: FTIR spectra of Mn\(_{0.0}Zn_{0.9}Sm_{x}Fe_{2-x}O_{4}\) (x =0.00, 0.01, 0.03 and 0.05)*

### 4.10.3. TEM analysis

The TEM micrograph of samples with Sm\(^{3+}\) content (x=0.03 and 0.05) annealed at 350\(^{0}\)C are shown in figure 3. It is clear that the particles are spherical in shape and are agglomerated. This agglomeration can be attributed to magnetic interaction arising among ferrite nano-particles. The particle size (DT) calculated from TEM, is larger than crystal size estimated by XRD, indicating that majority of particles in samples are multi-crystal particles.
The addition of Sm$^{3+}$ ions reduces the grain growth probably due to deposition of Sm$^{3+}$ on the grain boundaries which in turn hampers its motion [6].

*Figure 3: Transmission electron micrographs of Mn$_{0.6}$Zn$_{0.4}$Sm$_{x}$Fe$_{2.5}$O$_{4}$ (x = 0.03 and 0.05)*

4.10.4 Magnetic Properties by VSM

Figure 4 shows the magnetic hysteresis curves of the samples investigated by using vibrating sample magnetometer at room temperature with maximum applied field up to 1.5 T. It can be observed that very narrow hysteresis loops, reveals the behaviour of soft magnetic material. These features indicate the presence of super paramagnetic and single-domain particles for each of these ferrites [7]. From the Table 2, it can seen that the values of saturation magnetization ($M_S$), remanence magnetization ($M_r$), remanence ratio ($M_r/M_s$), and coercivity ($H_c$) and magneton number ($n_B$) are found to be decrease with increase in Sm$^{3+}$ ion concentration. According to Neel’s two sub-lattice model of ferrimagnetism, the net moment is given by the formula $\mu_B = M_B (x) - M_A (x)$, where $M_A$ and $M_B$ are the A and B sub-lattice magnetic moments in $\mu_B$ [8]. The existence of random canting of particle surface spins; surface effects and the occurrence of a glassy state have been reported to be playing an active role in the decline of magnetization values [9]. The magnetic moment decreases significantly in Sm$^{3+}$ substituted samples which can be attributed to small free ion of magnetic moment of Sm$^{3+}$, $n_B = 1.58\mu_B$ [10] as against for Fe$^{3+}$; $n_B = 5\mu_B$ at room temperature [11, 12]. The substituted Sm$^{3+}$ ion whose 4f and 5P electrons, occupies on octahedral site and hence Sm–Fe interaction is weaker than Fe–Fe interaction. This dilutes the interaction octahedral site and decreases the Curie temperature.
In ferrites, the coercive force obtained by reversal of the directions of the wall movement and that of domain rotation on reversing the direction of the applied magnetic field. Generally, the effective pinning for domain wall causes the coercivity; it is known that the larger grain size decreases $H_C$. In the present investigation, the coercive values are low; hence probability of domain rotation is also lower. The materials with larger grain size have been used to achieve lower core loss [13].

In the present work, the Y-K angles decrease with the increase in Sm$^{3+}$ ion concentration. The decrease in the Y-K angles suggests a decrease of triangular spin arrangements on B sites to produce the increment in A-B interaction. The effect of B-B interaction can be masked by strong A-B interaction to cause the spin on B sites to be aligned parallel to each other. However, the substitution of Sm$^{3+}$ seems to lead to canted type of arrangements on B sites to enhance the A-B interactions. Therefore, Sm$^{3+}$ substitution brings changes in magnetization, which can be attributed to the presence of Y-K angles in the spin system on B sites. The condition for Y-K angles to occur has been discussed from the consideration of the molecular field approximation using a noncolinear three sub-lattice model. [14,15].

Table I: Data on lattice parameter (A), Crystallite size ($D_p$) by XRD, Particle size (T) by TEM and Hopping length ($L_A$ and $L_B$) of Mn$_{0.4}$Zn$_{0.6}$Sm$_x$Fe$_{2-x}$O$_4$ ($x = 0.00, 0.01, 0.02, 0.03, 0.04, and 0.05$).

<table>
<thead>
<tr>
<th>Samarium concentration (X)</th>
<th>Lattice parameter (a) in Å</th>
<th>Crystallite size ($D_p$) by XRD in nm</th>
<th>Particle size (T) by TEM in nm</th>
<th>Hopping lengths octahedral site ($L_A$)</th>
<th>Hopping lengths Tetrahedral site ($L_B$)</th>
<th>absorption bands octahedral site V1</th>
<th>absorption bands Tetrahedral site V1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>8.344</td>
<td>27</td>
<td>30</td>
<td>3.613</td>
<td>7.226</td>
<td>350</td>
<td>529</td>
</tr>
<tr>
<td>0.01</td>
<td>8.410</td>
<td>16</td>
<td>18</td>
<td>3.641</td>
<td>7.283</td>
<td>358</td>
<td>537</td>
</tr>
<tr>
<td>0.03</td>
<td>8.412</td>
<td>13</td>
<td>14</td>
<td>3.642</td>
<td>7.285</td>
<td>372</td>
<td>544</td>
</tr>
<tr>
<td>0.05</td>
<td>8.417</td>
<td>10</td>
<td>12</td>
<td>3.644</td>
<td>7.289</td>
<td>380</td>
<td>546</td>
</tr>
</tbody>
</table>
Chapter-4

Synthesis and Studies of Structural and Magnetic Properties of Rare earth doped Mn-Zn ferrites

Table II: Data on Saturation magnetization ($M_S$), Remanence magnetization ($M_r$), Remanence ratio ($M_r/M_S$), and Coercivity ($H_C$), Magneton number ($\mu_B$), Anisotropy constant ($k$) and Y-K angle of Mn$_{0.4}$Zn$_{0.6}$Sm$_x$Fe$_{2.4}$O$_4$ ($x = 0.00, 0.01, 0.02, 0.03, 0.04$, and $0.05$).

<table>
<thead>
<tr>
<th>Samarium concentration ($X$)</th>
<th>Saturation Magnetization ($M_S$) in emu/gm</th>
<th>Remanent magnetization ($M_r$) in emu/gm</th>
<th>Coercivity ($H_C$) in Oe</th>
<th>Remanence ratio $M_r/M_S$</th>
<th>Magneton number ($\mu_B$)</th>
<th>Anisotropy constant ($K$) in erg/Oe</th>
<th>Yafet-Kittel angle $\alpha_{Y-K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>27.77</td>
<td>16.68</td>
<td>50.14</td>
<td>0.7148</td>
<td>1.703</td>
<td>1450</td>
<td>1.340</td>
</tr>
<tr>
<td>0.01</td>
<td>25.92</td>
<td>18.53</td>
<td>38.93</td>
<td>0.6491</td>
<td>1.589</td>
<td>1051</td>
<td>1.320</td>
</tr>
<tr>
<td>0.02</td>
<td>19.40</td>
<td>12.60</td>
<td>16.47</td>
<td>0.6006</td>
<td>1.189</td>
<td>333</td>
<td>1.247</td>
</tr>
<tr>
<td>0.03</td>
<td>18.13</td>
<td>10.82</td>
<td>11.01</td>
<td>0.5968</td>
<td>1.111</td>
<td>208</td>
<td>1.227</td>
</tr>
<tr>
<td>0.04</td>
<td>14.53</td>
<td>07.23</td>
<td>09.31</td>
<td>0.4975</td>
<td>0.891</td>
<td>141</td>
<td>1.183</td>
</tr>
<tr>
<td>0.05</td>
<td>12.85</td>
<td>05.81</td>
<td>04.10</td>
<td>0.4521</td>
<td>0.788</td>
<td>69</td>
<td>1.162</td>
</tr>
</tbody>
</table>

![Figure 4: Room temperature vibrating magnetometry study of Mn$_{0.4}$Zn$_{0.6}$Sm$_x$Fe$_{2.4}$O$_4$ where $x = 0.00, 0.01, 0.02, 0.03, 0.04$ and $0.05$](image)

4.10.5 Mössbauer spectroscopy analysis

All the synthesized samples were characterized by Mössbauer spectroscopy at room temperature (RT) in transmission geometry by using a constant-acceleration Doppler velocity drive with $^{57}$Co-source (Rh-matrix). The spectra were recorded by using a proportional counter.
Figure 5: RT Mössbauer measurements on $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Sm}_x\text{Fe}_{2.5}\text{O}_4$ (a) $x = 0.01$ (b) $x = 0.2$ (c) $x = 0.03$, (d) $x = 0.04$ (e) $x = 0.05$. 
The velocity of Mössbauer drive was calibrated using α-Fe foil at RT, which gives an isomer shift of -0.106 mm/s relative to the $^{57}\text{Co}$-source (Rh-matrix). The spectra obtained were least square fit using “NORMOS” program. The spectra after the least square fit are shown in Fig. 6. Mössbauer spectral parameters such as isomer shift ($IS$), quadrupole splitting ($QS$), magnetic hyperfine field ($B_{hf}$) and spectral area were obtained and tabulated in Table III. All the isomer shifts are given with respect to the $^{57}\text{Co}$-source (Rh-matrix). The distribution profiles of the magnetic hyperfine field parameters ($B_{hf}$) are plotted beside each Mössbauer spectrum.

The Mössbauer spectra of all the Mn$_{0.4}$Zn$_{0.6}$Fe$_{2-y}$Sm$_y$O$_4$ samples with $y = 0, 0.01, 0.03$ and $0.05$, recorded at RT are shown in Fig. 6. For the samples with $y = 0.0-0.03$, a Zeemann split broad (low intensity) sextet and a strong central doublet were seen. With increasing Sm-substitution, the sextet contribution seemed to disappear to an apparent doublet and for the the higher content od Sm$^{3+}$ only a central doublet has been observed. The line width of the central doublet was seen to be high in Sm=0.05 sample. This behaviour was unexpected for higher concentration of Sm, as the sample may behave like more superparamagnetic. Hence, this change in line width of the central doublet could not be explained only by a distribution of quadrupole doublets. Thus, the spectra corresponding to all samples were initially fit by distributions of sextets and doublets. Due to the limitation in assuming only a certain number of sub-spectra in the NORMOS program, the results showed majorly quadrupole split doublets which overestimate the paramagnetic behaviour. Thus, only distributions of sextets were then considered for the least square fit of the observed Mössbauer spectra. However, the results were erroneous, because the isomer shifts corresponding to the sextet distribution and the central doublet are different. Considering the decrease in particle size with Sm content in the samples and that in view of a strong central doublet seen regardless of the composition of the sample with slight increase in width, a distribution of sextets along with a crystalline doublet then considered as the fitting model for all the samples. During the least square fit to the observed Mössbauer spectra, the values of $IS$, $QS$ and line-width of the doublet for all samples were fixed to the approximate values of pure zinc ferrite ($IS = 0.235$ mm/s, $QS = 0.5$ mm/s and line width = 0.45 mm/s). The spectra after the fit are shown in Fig. 6 and resultant hyperfine parameters are listed in Table III.
Table III: Mössbauer spectral parameters obtained after the least square fitting of the Mössbauer spectra (Fig. 2) of Mn$_{0.5}$Zn$_{0.5}$Fe$_{2-y}$Sm$_y$O$_4$ samples. Average values of isomer shift ($\langle IS \rangle$) and magnetic hyperfine field ($\langle B_H \rangle$), quadrupole splitting ($QS$), relative spectral area and spectral line width (FWHM) are listed. Sub-spectra designated by S and D abbreviate for sextet distributions and doublet, respectively. The values of $IS$ are given with respect to the $^{57}$Co-source (Rh-matrix).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spectra type</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>$B_H$(T)</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>sextet distribution</td>
<td>0.24</td>
<td>-0.01</td>
<td>2.7</td>
<td>63.26</td>
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<tr>
<td></td>
<td>Doublet</td>
<td>0.24</td>
<td>0.40</td>
<td>-</td>
<td>36.74</td>
</tr>
<tr>
<td>F2</td>
<td>sextet distribution</td>
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<td>-0.04</td>
<td>3.6</td>
<td>60.63</td>
</tr>
<tr>
<td></td>
<td>Doublet</td>
<td>0.24</td>
<td>0.40</td>
<td>-</td>
<td>39.37</td>
</tr>
<tr>
<td>F3</td>
<td>sextet distribution</td>
<td>0.20</td>
<td>-0.05</td>
<td>3.6</td>
<td>62.74</td>
</tr>
<tr>
<td></td>
<td>Doublet</td>
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<td>0.39</td>
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<td>37.26</td>
</tr>
<tr>
<td>F4</td>
<td>sextet distribution</td>
<td>-0.206</td>
<td>-0.87</td>
<td>3.6</td>
<td>54.81</td>
</tr>
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<td>Doublet</td>
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<td>-</td>
<td>45.19</td>
</tr>
<tr>
<td>F5</td>
<td>sextet distribution</td>
<td>0.12</td>
<td>-0.21</td>
<td>3.6</td>
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</tr>
<tr>
<td></td>
<td>Doublet</td>
<td>0.25</td>
<td>0.39</td>
<td>-</td>
<td>37.16</td>
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</tbody>
</table>

4.11 Summary

Samarium substituted Mn-Zn nanoferrites were prepared by solution combustion. XRD analysis revealed that all the prepared samples shows single phase cubic spinel without any secondary phase. Increase in lattice constant value with samarium doping indicates the expansion of unit cell. The absorption bands in FTIR are found in the expected range of spinel ferrites. TEM images show the samples are spherical in shape and agglomerated. The magnetic behavior of pure and samarium doped magnesium ferrite particles shows soft ferrimagnetic nature. The decrease in saturation magnetization and remnant magnetization is attributed to the weak magnetic interactions. Mössbauer spectroscopy results suggest the existence of local disorder in the arrangement of cations in the sub-lattice of samples. Also, the pinning of magnetic moments was found to be solely due to Sm$^{3+}$ ions with related effects arising from particle size variation.
4.11 References