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Mössbauer Study of As Prepared and Gamma Irradiated $Mn_{0.7}Zn_{0.3}Fe_2O_4$ Nanoparticles

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Abstract: Nanoparticles of $Mn_{0.7}Zn_{0.3}Fe_2O_4$ were synthesized using normal combustion method. Nanoparticles were characterized using conventional tools like X-Ray Diffraction (XRD) for structural confirmation. Sample was irradiated with gamma radiation (200 Gy). Particle size was estimated from XRD data for both as prepared as well as irradiated sample. Mössbauer investigations were carried out at room temperature and the spectra were fitted with a doublet attributed to superparamagnetic nature and six magnetic sextets. The broader sextet is due to tetrahedral A–site and the other four are due to octahedral B–site. Isomer shift values are consistent with Fe^{3+} high spin state for all sites for both as prepared as well as for irradiated sample.

Keywords: Nanoparticles, X-Ray Diffraction, Infrared spectroscopy, Transmission electron micrograph, Mössbauer spectroscopy.

1 Introduction

Mn–Zn ferrites are the materials having wide range of technological applications in electronic industries as well as in the field of medical advancement and provide an opportunity to understand theoretically the interactions at nano-scale [1] The general formula of these materials is $(A)[B_2]O_4$, where the metallic cations in +2 state occupy the tetrahedral-A sites and the metallic cations in +3 occupy the octahedral-B site. In Mn-Zn Ferrite Zn is known to shows a strong affinity towards tetrahedral site where as Mn along with Fe occupies both tetrahedral and octahedral sites This unique cation distribution in mixed ferrites like Mn-Zn Ferrite governs various structural, magnetic as well as electrical properties of the material [2,3].

It is also reported that exposure to external factors such as high pressure, high temperature and high energy radiation/ particle beams can alter the properties of ferrite material. Especially high energy radiations such as gamma rays are known to produce drastic changes in structural, magnetic and electrical properties of Mn-Zn ferrite nanoparticles [4-8]. In present work we present results of X-ray diffraction XRD and Mössbauer investigations performed on as prepared and irradiated $Mn_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles prepared using combustion synthesis.

2 Experimental

2.1 Material Preparation

Nanopowders of $Mn_{0.7}Zn_{0.3}Fe_2O_4$ sample was synthesized using combustion synthesis. Metal nitrates and acetates were used as raw materials with Nitrilotriacetic acid as a complexing agent and Glycene as fuel for the preparation of sample [9-12]. The method has several advantages. Being simple it is cost effective, energy efficient and consumes less time.

2.2 Characterization

XRD patterns of $Mn_{0.7}Zn_{0.3}Fe_2O_4$ nanoferrites (as prepared and gamma irradiated) were obtained on Reghaku X-ray diffractometer (CuKα radiation, λ=1.5418Å). The Rietveld refined XRD data obtained on the sample was used for, particle size estimation using Sherrer's equation. Mössbauer spectra at room temperature were recorded using a Mössbauer spectrometer operated in constant acceleration mode (triangular wave) in transmission geometry. The source employed was Co-57 in Rh matrix of strength 50 mCi. The calibration of the velocity scale was done by using an enriched α-57Fe metal foil using a value of 331 kOe for the effective nuclear hyperfine field (H_{eff}) at room temperature. The recorded MS were fitted using the WinNormos fit program. The line width of calibration

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spectra is 0.23mms^{-1}. The results of isomer shift are relative to α-Fe metal foil.

2.3 Sample Irradiation with Gamma Rays.

Nanoparticles of $Mn_{0.7}Zn_{0.3}Fe_2O_4$ ferrite sample was exposed to gamma radiation (200 Gy). The gamma radiation of wavelengths λ_1= 0.0106 Å with energy E_1= 1.17Mev and λ_2= 0.009 Å with energy E_2= 1.33Mev obtained from ^{60}Co source were used to irradiate nanoparticle ferrite samples.

3 Results and Discussion

3.1 X-Ray Diffraction

The Rietveld refined X-Ray diffraction patterns of as prepared and gamma irradiated $Mn_{0.7}Zn_{0.3}Fe_2O_4$ nanoferrites are shown in Figure 1 and 2, respectively. The Rietveld analysis of XRD patterns confirms the single-phase formation of samples in the cubic spinal crystal structure under the space group Fd3m.

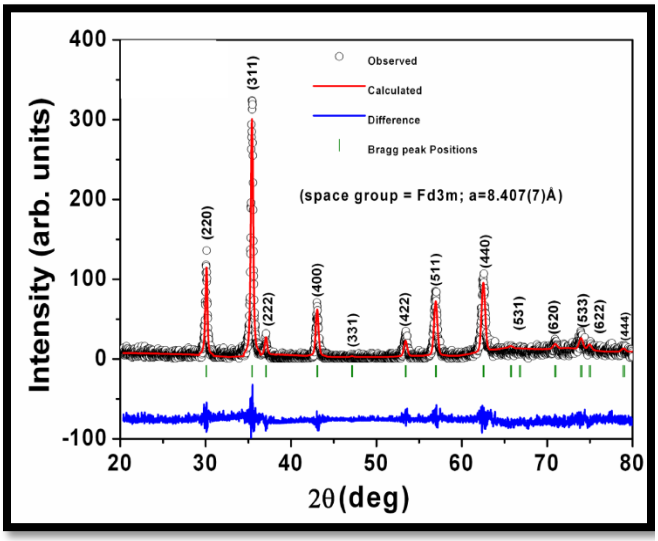

Fig.1: Rietveld analysis of as prepared $Mn_{0.7}Zn_{0.3}Fe_2O_4$ sample.

Lattice constant value was determined from Rietveld refinement of the XRD pattern by using FULLPROF. Lattice constant value was found to be 8.407(2) Å for as prepared sample and 8.394(4) Å for gamma irradiated sample. This decrease can be attributed to various reasons such as the lattice vacancies generated after irradiation [13], also be due to irradiation produced the compressive strain and the broadening of peaks along with the reduction in peak intensity [14-18].

The average particle size determined using Scherer's formula (Eq.1) was found to be 23 nm and 18 nm for as prepared and gamma irradiated $Mn_{0.7}Zn_{0.3}Fe_2O_4$ ferrite nanoparticles, respectively. Sherrer's equation is given by

$$Particle\ Size\ 't' = \frac{0.9\lambda}{\beta Cos\theta} \quad (1)$$

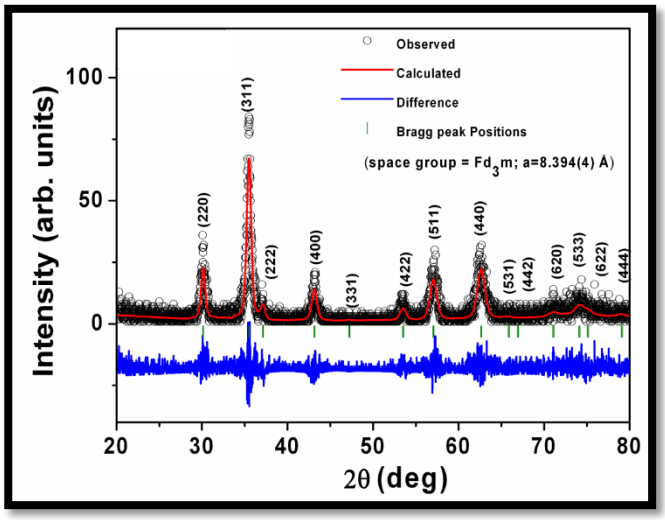

Fig. 2: Rietveld refined XRD patterns of gamma irradiated $Mn_{0.7}Zn_{0.3}Fe_2O_4$ nano ferrites.

Where λ is the wavelength of X-rays, β is full width at half maxima of X-ray diffraction peaks, θ is the angle of Bragg diffraction.

3.2 Mössbauer Spectroscopy

In order to identify the exact oxidation state and local environment of Fe as well as the magnetic state and cation distribution in both as prepared as well as in irradiated sample at room temperature, we have carried out a Mössbauer study. Mössbauer spectrum of as prepared and gamma irradiated $Mn_{0.7}Zn_{0.3}Fe_2O_4$ was recorded at 300K in the velocity range of -11.5 to 11.5 mm/s and is shown in Figure 3.

Mössbauer spectra were fitted by a WinNormos fit program assuming Lorentzian line shapes where in open circles are the experimental data and the solid lines are the fitted data.

Mössbauer spectra wer fitted with a doublet and six sextets (Zeeman patterns). The analysis results of Mössbauer spectra in form of Mössbauer parameters are given in Table 1. The low isomer shift values for sextet B for as prepared and irradiated samples are attributed to tetrahedral site with high spin Fe in +3 states. Isomer shift values for remaining five magnetic sextets are also consistent with existence of high spin Fe^{3+} in octahedral sites [19,20]. The relatively splitting values for doublets (0.612 and 0.501 mm/s) in both the samples (as prepared and gamma irradiated) indicate comparatively higher asymmetry.

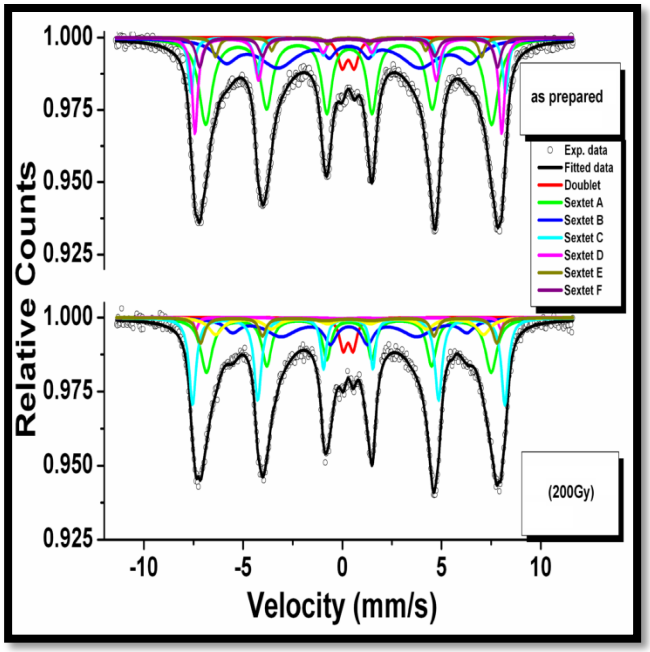

Fig.3: Mössbauer spectra of as prepared and gamma irradiated $Mn_{0.7}Zn_{0.3}Fe_2O_4$ ferrite nanoparticles recorded at room temperature (300K).

larger δ for octahedral sites corresponds to lower s-electron density at the Fe nucleus and hence may indicate a larger internuclear separation. Consistently high Quadruple Non-zero quadrupole splitting can be attributed to chemical disorder. As a result an electric field gradient (EFG) of varying magnitudes, directions, sign and symmetry is produced which results in a distribution in the quadrupole shift. The line width values of both spectra are found to have values that are 3 times higher from the instrumental line width. These higher values of line width (broad line) indicate the nano size particles of $Mn_{0.7}Zn_{0.3}Fe_2O_4$ sample [21]. On the basis of Mössbauer results, the cations distribution is found and is presented in Table 2.

It is observed that concentration of Fe in Octahedral site has increased from 73.2 percent to 75.28 percent after gamma irradiation. This transfer of Fe on shows great affinity towards octahedral site and this tendency is seen at greater extent in irradiation sample. Transfer of Fe on octahedral site is compensated transfer of Mn from octahedral site to tetrahedral site where as Zn in +2 state shows affinity towards tetrahedral site in both as prepared and irradiated sample.

Table1: The hyperfine field values (H_{hf}), isomer shift (δ), quadrupole splitting (Δ), line width (Γ), relative area (R_A) of tetrahedral and octahedral sites of Fe^{3+} ions for $Mn_{0.7}Zn_{0.3}Fe_2O_4$ ferrite nanoparticles derived from Mössbauer spectra recorded at room temperature.

$Mn_{0.7}Zn_{0.3}Fe_2O_4$	Iron site	Isomer shift (δ) mm/s	Quadrupole splitting (Δ) mm/s	Hyperfine field (H_{hf}) Tesla	Relative area, (R_A) (%)	line width (Γ) mm/s
As prepared	Doublet (S. P.)	0.294±0.011	0.612±0.021	-	1.41	0.510±0.001
	Sextet (A) (Octa)	0.338±0.085	-0.039±0.002	44.69±0.85	39.60	0.616±0.011
	Sextet (B)(Tetra)	0.298±0.012	-0.307±0.007	38.18±0.87	26.80	0.666±0.016
	Sextet (C) (Octa)	0.282±0.036	0.046±0.021	49.17±0.98	5.01	0.364±0.107
	Sextet (D) (Octa)	0.373±0.038	0.046±0.006	47.93±1.12	9.92	0.434±0.056
	Sextet (E) (Octa)	0.320±0.025	-0.099±0.019	41.58±1.03	2.46	0.363±0.011
	Sextet (F)(Octa)	0.317±0.011	0.007±0.001	46.45±0.68	14.80	0.791±0.112
Gamma Irradiated (200Gy)	Doublet (S. P.)	0.294±0.020	0.501±0.021	-	1.43	0.432±0.038
	Sextet (A) (Octa)	0.336±0.019	-0.018±0.019	44.49±0.11	22.84	0.511±0.203
	Sextet (B)(Tetra)	0.309±0.010	0.038±0.068	36.64±1.33	24.72	0.753±0.121
	Sextet (C) (Octa)	0.309±0.017	0.029±0.016	48.81±0.01	15.50	0.335±0.221
	Sextet (D) (Octa)	0.607±0.125	-0.790±0.198	47.63±0.69	4.75	0.751±0.112
	Sextet (E) (Octa)	0.353±0.018	0.031±0.036	41.87±0.37	12.36	0.815±0.238
	Sextet (F) (Octa)	0.308±0.145	0.027±0.002	46.29±0.25	18.40	0.498±0.111

Table 2: Cation distribution estimated from Mössbauer spectroscopy study for as prepared and gamma irradiated $Mn_{0.7}Zn_{0.3}Fe_2O_4$ ferrite nanoparticles. [( )$_A$: tetrahedral site, [ ]$_B$:octahedral site.]

$Mn_{0.7}Zn_{0.3}Fe_2O_4$	A-site (%) of Fe ions	B-site (%) of Fe ions	Cation distribution
As prepared	26.8	73.2	$(Fe_{0.54}Mn_{0.26}Zn_{0.3})_A[Mn_{0.44}Fe_{1.46}]_BO_4$
Gamma Irradiated (200Gy)	24.72	75.28	$(Fe_{0.49}Mn_{0.31}Zn_{0.3})_A[Mn_{0.39}Fe_{1.51}]_BO_4$

4 Conclusions

Nanoparticles of $Mn_{0.7}Zn_{0.3}Fe_2O_4$ were synthesized using combustion synthesis. As prepared samples were characterized and gamma irradiated with a radiation dose of 200Gy. Both as prepared and gamma irradiated samples investigated with Mössbauer spectroscopy to study the effect of high energy radiation on structural parameters, cationic distribution and also identify the exact state of Fe in both tetrahedral site and octahedral site before and after gamma irradiation. Reduction of lattice constant and decrease in particle size were observed as the direct consequences of gamma exposure. Low values of Isomer shift and non-zero quadruple splitting for both as prepared as well as gamma radiated samples are evident for the preferred existence of Fe in +3 oxidation state. High Quadruple splitting values for doublets in both the samples (as prepared and gamma irradiated) indicate comparatively higher asymmetry. Due to preferred +3 oxidation state, Fe shows great affinity towards octahedral site and this tendency is seen at greater extent in irradiation sample. Transfer of Fe on octahedral site is compensated by transfer of Mn from octahedral site to tetrahedral site where as Zn in +2 state shows affinity towards tetrahedral site in both as prepared and irradiated sample.

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