**57 Fe Mössbauer investigation of nanostructured zinc ferrite irradiated by 100 MeV oxygen beam**

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Abstract. Zinc ferrite nanoparticles of different size were irradiated in vacuum with 100 Mev O⁷⁺ ion beam at a fluence of 5\times10¹³ ions/cm². Presence of ZnO phase was observed after the irradiation in the samples. ⁵⁷Fe Mössbauer spectroscopy shows the presence of well defined doublets in case of pristine and irradiated samples which are the attributes of superparamagnetism in the specimen. The variation of Mössbauer hyperfine parameters is discussed.

1. Introduction

Mössbauer spectroscopy is well known to study the swift heavy ion (SHI) induced effects in ferrites [1-3]. The SHIs lose energy in the target mainly by two means (i) electronic energy loss \(dE/dx_e\), and (ii) nuclear energy loss \(dE/dx_n\). The dominancy of electronic energy loss, as in present case, leads to the creation of variety of defects, phase change like amorphization [4-6] etc.

Ferrite materials have numerous applications in various electromagnetic devices [2,7], ferrofluid technology, magnetic diagnostic and spintronics devices [8]. Among all the ferrites, zinc ferrite having normal spinel structure in bulk behaves as paramagnetic at room temperature and as antiferromagnetic below 10 K [9]. It has been observed that the various nonequilibrium processing methods [10-15] result in disordered zinc ferrite inducing the nanophasic in the system.

Production and modification of nanostructures by SHI is a work of great importance [16]. It is believed that the presence of defects induced by SHI influence the magnetic and related properties of these systems [17- 19]. In the present work we have reported the results obtained from Mössbauer study of zinc nanoferrite irradiated by the 100 MeV oxygen beam.

2. Experimental

Zinc ferrites nanoparticles of different size have been prepared by using the combination of nitrates of appropriate cations and citric acid. The molar ratio of cations to citric acid was taken as 1:3. The stoichiometric proportion of zinc nitrate and ferric nitrate were dissolved in distilled water. Citric acid solution was made separately. These solutions were mixed thoroughly and the solution was then heated at 85°C with continuous stirring for 2h. The heated solution was allowed to cool at room temperature and finally it was dried at 100°C for overnight in an oven to form the precursor material.
This precursor material was sintered at various temperatures ranging from 400°C to 1000°C for 1h to get pristine samples of nanostructured zinc ferrite. The pristine samples were irradiated in vacuum with 100 MeV O⁷⁺ ion beam at the fluence of 5×10¹³ ions/cm² using 15 UD Pelletron Accelerator at Inter University Accelerator Centre, New Delhi. The structural and morphological characterization of pristine and irradiated samples have been done by using a Bruker AXS D8 Advance X-ray diffractometer and JEM 1011 transmission electron microscope. The Mössbauer spectra of the samples were recorded at room temperature in transmission geometry using 25mCi ⁵⁷Co-in-Rh matrix. The spectra were analyzed using the NORMOS/SITE programmes. The isomer shift values are reported with respect to standard natural iron foil.

3. Results and Discussion.

Fig 1 shows few representative XRD spectra of the pristine and irradiated samples. It is observed that pristine samples exhibit pure spinel phase, however some small trace of ZnO phase also present in the irradiated samples. This may be due to the deterioration of ordered spinel structure after the irradiation. SRIM calculation shows the values of electronic stopping, nuclear stopping and projected range as \( S_e = 1.09 \text{ keV/nm}, S_n = 0.618 \text{ eV/nm} \) and \( R_p = 65 \mu\text{m} \) respectively. The target volume is \( 4.7 \times 10^{-3} \text{ cm}^3 \) and was spread uniformly in the grooves of 1 cm diameter supported by Aluminium foil. The thickness of the spreaded powder was less than the projected range. Hence, there is no chance of implantation. The threshold electronic stopping for producing the columnar defects in zinc ferrite is ~ 13 keV/nm [20]. Hence, we do not expect any columnar defect in the irradiated system.

\[ \text{Figure 1: XRD spectra of the pristine and irradiated samples of sintered at (a) 400°C and (b) 800°C.} \]

\[ \text{Figure 2. Crystallite size of the pristine and irradiated samples.} \]

\[ \text{Figure 3. Lattice parameter of the pristine and irradiated samples.} \]

The crystallite size and lattice parameters of the pristine and irradiated samples were estimated [21] and are shown in figures 2 and 3. The crystallite size varies from 12 nm to 62 nm as the sintering temperature varies from 400°C to 1000°C. The respective values for the irradiated samples are 10 and
42 nm and the variation with sintering temperature is almost similar to that of pristine sample. The decrease in the crystallite size of the irradiated samples is attributed to the hammering effect of SHI beam. We observe that there is no regular trend of variation of lattice parameter with sintering temperature of the irradiated specimen (figure 3). Figure 4a and 4b show the representative transmission electron micrographs of the pristine and irradiated samples having sintering temperature of 500°C. The average particle size obtained from TEM is ~ 21 nm for the pristine and ~13 nm for the irradiated samples. TEM also shows the reduction of particle size after irradiation.

![Transmission Electron Micrographs](image)

**Figure 4**: Transmission Electron Micrographs of the (a) pristine sample sintered at 500°C and (b) its irradiated counterpart (fluence=5×10^{13} ions/cm^2 (5E13)).

Figure 5 shows few representative Mössbauer spectra of samples at room temperature. All the recorded spectra show well defined doublet, which may be a signature of presence of superparamagnetism in both the pristine and irradiated samples [22, 23] as supported by VSM study of our previous work [22].

![Mössbauer spectra](image)

**Figure 5.** Mössbauer spectra of the pristine and irradiated samples.

**Figure 6.** Variations of I. S. (±0.005), Q. S. (±0.005) and L.W.D. (±0.01) of the pristine and irradiated samples.

The values of isomer shift are of the order of 0.31 mm/s for the pristine sample except for the sample sintered at 400°C (I. S. = 0.34 mm/s). These values increase after the irradiation and ranges from 0.36 to 0.39 mm/s. The excess amount of energy induced by swift heavy ion in the system is confined in form of heat within grain volume [24,25]. This may give rise to thermal expansion and excitation of the electronic state, consequently, the values of I.S. increases [26]. The values of isomer shift for the pristine and irradiated samples are characteristics of Fe^{3+} charge state (figure 6) [27]. The value of quadrupole splitting decreases form 0.44 mm/s to 0.41 mm/s for the pristine sample and increase from 0.37 mm/s to 0.40 mm/s for the irradiated samples as the sintering temperature increases from 400°C to 1000°C (figure 6). We observe decrease in Q.S. after the irradiation. The decrease in the value of Q. S. is attributed to the less cation inversion, creation of oxygen vacancies [28, 29]. Line-width for the pristine sample seems to be almost constant within experimental error at a value of 0.40 mm/s, while the irradiated sample has very much different trend (figure 6). The line width (L.W.D.) decreases first upto the sintering temperature of 700°C, and then increases abruptly upto 1000°C.
decrease in the line-width after irradiation may be attributed to the reduction of surface strain or domain pinning. This type of behaviour was observed by previous workers also [20].

Conclusion
The structural characterization by using XRD shows the appearance of ZnO phase in the system after the irradiation. The particle size of the irradiated samples decrease with respect to irradiated counterpart. We also found that the nanostructured system remain in same superparamagnetic state after the irradiation.

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References
[1] Studer F, Nguyen N, Fuchs G and Toulemonde M 1986 Hyperfine Interactions 29 1287
[2] Costantini J M, Studer F, Peuzin J C 2001 J. Appl. Phys. 90 126
[3] M. C. Chhanbar, K. B. Modi, C. J. Baldha, H. H. Joshi, R. V. Uppaydhyay and Ravi Kumar, Nuclear Instr. and Methods in Physics Research B 244 (2006)124-127
[4] Studer F and Toulemonde M 1992 Nucl. Instr. Meth. Phys. Res. B 65 560
[5] Szenes G 1995 Phys. Rev. B 51 8026
[6] Goya G F, Rechenberg H R, Chen M, Yelon W B 2000 J. Appl. Phys. 87 8005
[7] T. Pannaparayil, S. Komarneni, R. Marande, M. Zadarko, J. Appl. Phys. 67 (1990) 5509
[8] L. Lu, M. L. Sui and K. Lu, Science, 287, (2000)1463
[9] Pettit G. A. And Forester D. W. 1971 Phys. Rev. B 4 3912
[10] Chinnasamy C N, Narayanasamy A, Ponpandian N, Chattopadhyay K, Guerault H, Greenech, J-M 2000 J. Phys: Condens Matter 12 7795
[11] Oliver S A, Hamdeh H H and Ho J C 1999 Phys. Rev. B 60 3400
[12] Sato T, Haneda K, Seki M and Iijima T 1990 Appl. Phys. A 50 13
[13] Jaydevan B, Tohji K, and Nakatsuka K 1994 J. Appl. Phys. A 76 3625
[14] Nakashima S, Fujita K and Hirao K 2005 J. Phys: Condens Matter 17 137
[15] Yamamoto Y, Tanaka H and Kawai T 2001 Jpn J. Appl. Phys., Part 2 40 L545
[16] Pivin J-C 2005 Material Science-Poland 23 101
[17] Sharma S K, Ravi Kumar, Kumar V V S, Knobel M, Reddy V R, Gupta A and Singh M 2006 Nucl. Instr. Meth. in Phys. Res B 248 37
[18] Rao B P, Rao K H, Rao P S V S, Kumar A M, Murthy Y L N, Ashokan K, Kumar V V S, Ravi Kumar, Gajbhiye N S and Caltum O F 2006 Nucl. Instr. Meth. in Phys. Res B 244 27
[19] Taylor R H 1975 Adv. Phys. 24 68
[20] Ravi Kumar, Sharma S K, Dogra A, Shivakumar V V, Dolia S N, Gupta A, Knobel M and Singh M 2005 Hyperfine Interaction 160 143.
[21] B. D. Cullity-Introduction to X-ray diffraction (Addision-wesley, Newyork, 1972)
[22] Singh J P, Srivastava R C, Agrawal H M and Kushwaha R C 2008 Hyperfine Interaction 183 221
[23] Roy M K, Halder B and Verma H C 2006 Nanotechnology 17 232
[24] Ghosh S, Gupta A, Ayub P, Kumar N, Khan S A, Banerjee D and Bhattacharya R 2004 Nucl. Instr. Meth. Phys. Res. B 225 310
[25] Chen G 2000 J. Nanoparticle Research 2 199
[26] Uppadhyay C and Verma H C 2004 Appl. Phys. Lett. 85 2074
[27] Ehrhardt H, Campbell S J, Hoffmann M 2002 J. Alloy Componds 339 25
[28] Roy M K and Verma H C 2006 J. Magn. Magn. Mater. 306 98
[29] Li F S, Wang L, Wang J B, Zhou Q G, Zhou X Z, Kunkal H P, Williams G 2004 J. Magn. Magn. Mater. 268 332