Mössbauer studies of nanocrystalline ZnFe$_2$O$_4$ particles prepared by spray pyrolysis method.

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Abstract. This paper reports the synthesis and characterization of nanoparticles of Zn Fe$_2$O$_4$ by spray pyrolysis method. XRD studies indicates that the particle formed are ultra fine (20 nm) associated with strain. The particle size is confirmed by TEM analysis. The room temperature Mossbauer spectrum shows only a doublet which could be indicative of either paramagnetic or superparamagnetic phase. The value of isomer shift is in the range 0.34±0.01 mm/s while quadruple splitting is in the range 0.48±0.01 mm/s. A series of low temperature studies has been performed and the spectra obtained at 20 K and 5K show the presence of two well resolved sextets, which are attributed to the Fe$^{3+}$ ion in the tetrahedral and octahedral sites of the spinel structure. The application of external magnetic field yields a better fitting resolution of the sub spectra between A and B sites. The temperature dependant and in-field measurements yielded valuable insights about magnetic phase (superparamagnetic), local cation distribution among A sites and B sites, inversion parameter (δ =0.74), canted spin alignment ($\psi_A = 29.58$, $\psi_B = 48.46$) and the blocking temperature ($T_B = 50$ K).

1. Introduction
Magnetic nanoparticle synthesis has received wide research interest due to its unusual magnetic properties compared to other spinel ferrites. Zinc ferrite with nano size shows cation inversion which in turn affects its magnetic characteristics, like super paramagnetic relaxation time, blocking temperature. The inversion parameter δ is used to indicate the degree of inversion in the sample [1-3]. The cation inversion among crystallographically identical sites present in normal spinel ferrites were found to be affected by preparation methods and particle size distribution. The purpose of the present work is to estimate particle sizes and magnetic characteristics of zinc nanoferrites, synthesized by
spray pyrolysis of polymer precursor—a simple, rapid and low temperature method and but rarely reported [4-12].

2. Experimental

Synthesis of the zinc ferrite nanoparticles was done by spray pyrolysis of polymer precursor prepared by taking high purity zinc nitrate (Merck), ferric nitrate (Loba) and Polyvinyl Alcohol (PVA) as starting materials. The presence of PVA helps the homogenous distribution of the metal ions in their polymeric network structure and inhibits their segregation/precipitation from the solution. The resulting viscous mixture of PVA metal nitrates is spray dried around 130°C to obtain a brown fluffy powder. The powders were subsequently heat treated at 450°C for 20 minutes for synthesizing desired metal oxides. Five such samples were prepared (Z1, Z2, Z3, Z4, and Z5) with varying molar ratios. The crystalline phase of nanoferrites was analyzed by XRD (Cu Kα radiation λ =1.5406Å) and transmission electron microscope (TEM) operating at 300kV. ⁵⁷Fe Mossbauer measurements with ⁵⁷Co radioactive source in constant acceleration mode were done for identifying the magnetic phases in the samples.

3. Results and discussion

3.1 XRD and TEM Studies

The XRD patterns of five molar fractions show well-resolved peaks, which confirm polycrystalline and monophasic nature of the prepared material. The peaks corresponding to planes (220), (311), (222), (400), (422), (511), (440) provide a clear picture for the formation of spinel structure of the ferrite [13]. However, the pyrolytic decomposition process of ferrite powders is a chemically complicated process in which many intermediate products can be formed. The phases that may be present in the sample are ZnO, Fe₂O₃, Fe₁₋ₓO and stochiometric ZnFe₂O₄ [14]. The XRD pattern of the fifth fraction (Z5) seems to be free from impure phases and hence Z5 has been chosen for further studies. The lattice parameter ‘a’ of Z5 determined as 0.8447nm matches well with JCPDS (00-022-1012) file for ZnFe₂O₄. The grain size of the zinc nanoferrite is determined using Scherrer’s equation and is around 20nm. The full width at half maximum (FWHM) value of the peak corresponding to (311) plane is chosen for calculating the particle size. TEM image given in figure 1(a), reveals a narrow particle size distribution and support the average particle size estimated by XRD. Furthermore, the selected area electron diffraction pattern (figure 1(b)) of the same sample shows strong spotty ring patterns, indicating a highly crystalline spinel structure.

![Figure 1(a) TEM picture of Z5](image1)
![Figure 1(b) SAED pattern of Z5](image2)

3.2 Mossbauer study

The temperature depended Mossbauer spectrum (MS) of the 20nm sample has been studied and the nuclear quadruple splitting of ⁵⁷Fe and there are no magnetic hyperfine interactions. The value of
isomer shift is in the range 0.34 ± 0.01 mm/s while quadrupole splitting (QS) is in the range 0.48 ± 0.01 mm/s[15]. The QS value indicates a strong electric field gradient around $^{57}$Fe nuclei and may be attributed to large surface to volume ratio in nanoparticles, though the bulk material has cubic symmetry [16]. When the temperature is reduced to 90K, a weak sextet pattern appears in addition to the reduction of the intensity of the doublet pattern. The sextet component increases as the spectra obtained are shown in figure 2. The room temperature spectrum shows only a doublet pattern due to temperature decreases to 50K. At 20K the doublet component disappears and only the sextet pattern remains. This typical behaviour of Mossbauer spectra can be attributed to superparamagnetism(SPM)- a unique character of magnetic nanoparticles. MS is a powerful tool to characterize magnetic nanoparticles undergoing SPM relaxation since its experimental measurement time ($\tau_L$) is around relaxation time ($\tau$), determined by the equation

$$\tau=\tau_0 \exp(KV/k_B T)$$  \hspace{1cm} (1)

where $\tau_0$ ($10^{-9}$ to $10^{-10}$s) is the inverse of natural frequency of gyromagnetic precession, K is anisotropic energy constant, V is the volume of the particle, $k_B$ is the Boltzmann constant, T is the Kelvin temperature. When the relaxation time $\tau$ is smaller than $\tau_L$ the fluctuation of the particle magnetization direction is so rapid that the average of internal magnetic hyperfine field is zero at $^{57}$Fe nucleus site. Consequently there is only a quadrupole doublet splitting in the spectrum. But, when $\tau$ approaches $\tau_L$, a sextet pattern can emerge. However, some $^{57}$Fe nuclei still experience a rapid superparamagnetic relaxation and the doublet pattern remains visible. When the temperature is low enough, the relaxation in the nanoparticles are much slower and the spectrum becomes a pure sextet pattern. The characteristic temperature indicating the onset of the blocking process is called blocking temperature ($T_B$). Its value falls between 50K and 20K & which is not only much higher than that reported for nanoparticles but also the transition occurs over a much wider temperature range. The origin for the large increase in $T_B$ for zinc nanoferrite (ZNF) particles is most likely attributable to redistribution of Fe and Zn cations on A and B sites, a fact which is confirmed by $\delta$ – the inversion parameter[17-20]. The assignment of cation sites and determination of area ratio can be obtained from spectra recorded at 5K with and without field. The data obtained for the cation distribution between the A and B sites are given in Table 1 and those data have been used for extracting the value of $\delta$ - an index for cation distribution among A and B sites - using the equation

$$I_{(A)}/I_{(B)} = (f_{(A)}/f_{(B)})[\delta/(2-\delta)]$$  \hspace{1cm} (2)

where $I_{(A)}$ and $I_{(B)}$ are the sub spectral intensities of A site and B site and the ratio of recoil free fractions of A and B sites , $f_{(B)}/f_{(A)} =1$ at 5K. The calculated value of degree of inversion is 0.74.
Based on the δ value, the cation distribution in the spray pyrolytically synthesized zinc nanoparticles are \{Zn\textsubscript{0.74}Fe\textsubscript{0.26}\} & [Zn\textsubscript{0.26}Fe\textsubscript{1.74}] \textsubscript{O\textsubscript{4}}. The δ value of ZNF supports the redistribution of zinc cation to the octahedral sites. [21-24].

**Figure 2.** Mossbauer spectra obtained at different temperatures for ZnFe\textsubscript{2}O\textsubscript{4}

Mossbauer spectroscopy is a powerful tool for extracting the orientation of the internal magnetic field. The average canting angle between the external field and the A or B site Fe\textsuperscript{3+} hyperfine field directions were calculated from the ratio of the intensities of lines 2 and 3 from each sub spectra, $I_2/I_3$, according to Tuck et al., [25]

$$\psi = \arccos\left[\frac{4 - I_2/I_3}{4 + I_2/I_3}\right]^{1/2}$$ (3)
The value of $\langle \psi \rangle$ is listed in Table 1. The values are different from the reported values [26] and the variations may be attributed to the dependence of magnetic properties on method of preparation and the particle sizes.

Table 1. Fitted parameters of Mossbauer spectra at 5K with and without field $H=5T$ for Z5 sample.

| Sample | site | Rl.Area % | $H_0(T)$ | $H(T)$ | $I_2/I_3$ | $\langle \psi \rangle$ |
|--------|------|-----------|----------|--------|-----------|----------------|
| Z5     | A    | 37        | 52.8656  | 56.56  | 0.55487   | 29.58         |
|        | B    | 63        | 50.3024  | 49.39  | 1.55602   | 48.46         |

4. Conclusion
Spray pyrolysis method has been used to synthesize nanophasic zinc ferrite. XRD results indicate that the particles formed are ultrafine (20nm) associated with strain. A temperature dependent Mossbauer spectroscopy has been used for elucidating the magnetic properties of the ZNF particles. MS—a unique technique that is able to distinguish between equivalent crystallographic sites and to reveal the non co-linearity of the spin arrangement present in spinel structure—has been effectively employed and its results gave valuable insight about magnetic phase (super paramagnetic), local cation distribution between A sites and B-sites, inversion parameter ($\delta=0.74$), canted spin alignment ($\psi(A)=29.58$, $\psi(B)=48.46$) and the blocking temperature ($T_B=50K$).

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References
[1] Kamiyama T, Haneda K, Sato T, Ikeda S and Asano H January 1992 Solid State Commun. 81 p563
[2] Sato T, Haneda K, Seki N and Iijima T 1990 Appl. Phys. A 50 p13
[3] Jayadevan B, Tohji K and Nakatsuka K 1994 J. Appl. Phys. 76 p 6325
[4] Mahamoud M H, Hamdeh H H, Ho J C, O’shea M J and Walker J C 2000 J.Magn. Magn. Mater. 220 pp 139-146
[5] Atif M and Hasanian S K 2006 Solid state Commun. 138 pp 416-424
[6] Marykkutty Thomas and George K C 2009 Indian J. of Pure and applied physics. 47 pp 81-86
[7] Saez Puche R, Torralvo Fernandez M J, Balanco Gutierrez V, Gomez R, Marquin V, Marquina M L, Perez Mazariego J L and Ridaura R. 2008 Bol.Soc.Esp.Cream. 47 pp 3133-137
[8] Pramanik P 1996 Chemical synthesis of nanosized Oxides. Bull.Mater.sci. 19 pp 957-961
[9] Ghosh N N 2002 Mat. Res. Soc. Symp. Proc.720
[10] Xinyu Zhao, Baicun Zheng, Hongchen Gu, Chunzhong Li, Shi Chang Zhang, Darrell Ownby P 1999 J. mat. Res. 14 pp 3073-3082
[11] Pedro Tartaj, Mar´ del Puerto Morales, Sabino Veintemillas-Verdaguero, Teresita Gonz´alez-Carre ´no and Carlos J Serna 2003 J. Phys. D: Appl. Phys. 36 R182–R197
[12] Drofenik M, Lisjak D and Makovec D 2005 Materials Science Forum 494 pp 129-136
[13] Cross W B, Affleck L, Kuznetsov M V, Parkin I P and Pankhurst Q A 1999 J. Mater. Chem. 9
2545

[14] Yao Li, Jiupeng Zhao, Jiuxing Jiang and Jiecai Han 2003 Materials Research Bulletin 38 pp 1393–399

[15] Evans B J, Hafner S S and Weber H P 1971 J.Chem.Phys. 55 p 5282

[16] Mandal K, Pan Mandal S, Agudo P and Pal M 2001 Appl.Surface Sci. 182 p386

[17] Blanco-Gutierrez V, Torralvo M J, Saez-Puche R and Bonville P 2010 J.phys 200 072013

[18] Krupicka S and Novak P in:E.P.Wohlfarth(ed.) 1982 Ferromagnetic Materials 3 p194

[19] Morrish A H 2001, The Physical principles of Magnetism, (New York: IEEE press) p 504

[20] Smit J and Wijn H P J 1959 Ferrites (New York: Wiley) p 150

[21] Morrish A H and Clark P E 1975 Phys.Rev.B 11 p 278.

[22] Sawatzky G A, Van Der Woude F and Morrish A H 1969 Phys.Rev.183 p 383

[23] Goya G F and Rechenberg H R 1999 J.Magn.Magn.Mater 196-197 191

[24] Oliver S A, Harris V G, Hamdeh H H and Ho J C 2000 Appl.Phys.Lett. 76 p 2761

[25] Tuek J and Zbaril R 2005 Czech.J.Phys. 55 p 893

[26] Li F S, Wang L, Wang J B, Zhou Q G ,Kunkel H P and Williams G 2004 J.Magn.Magn.Mat. 268 pp 332-339