Effect of thermal treatment on the magnetic properties of nanostructured zinc ferrite

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Abstract. Present report elucidates the effect of sintering time (2 and 3h) and temperature (300, 400, 500 and 600°C) on the magnetic properties of zinc ferrite nanoparticle. XRD shows the presence of cubic spinel phase in the samples. The average crystallite sizes of the samples increase with the sintering temperature and sintering time. The Mössbauer and VSM measurements show the presence of superparamagnetic/paramagnetic phase of the samples.

1. Introduction
Zinc ferrite, one of the most important binary oxides, offers an excellent opportunity for its use in electrical, semiconductor, radio engineering, automatics and radio technology [1]. Bulk zinc ferrite exhibits normal spinel structure with all zinc ions on A-site and all ferric ions at B-site and is paramagnetic at room temperature having Néel temperature of 10 K[2].

The magnetic properties of zinc ferrite are significantly affected when some amount of Fe transfers to tetrahedral site [3]. This distribution of cations in zinc ferrite results when the particle size approaches to nanoregime by using various methods of synthesis [4-12]. The magnetic properties of this system is believed to arise due to the formation of superparamagnetic domains [11-13], coexistence of ferrimagnetic and antiferromagnetism at room temperature [14] and spin-glass state [4]. Hence, the exact cause responsible for these properties is still not clear.

2. Experimental
Zinc ferrite nanoparticles have been prepared by using the nitrates of appropriate cations and citric acid. The cations to citric acid molar ratio were taken as 1:3. The solution was 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. The precursor was sintered for 2 and 3 h at 300, 400, 500 and 600°C. For convenience the samples are coded as ZFt-T (where, ZF, t and T refer to zinc ferrite, sintering time and sintering temperature respectively).

The observation of crystalline phase and structure of the synthesized specimens were made with the help of BRUKER AXS D8 Advance XRD diffractometer using Cu-Kα radiation (λ=1.54Å). TEM micrographs of these samples were recorded on JEM-1011 transmission electron microscope in order to determine the morphology and particle size of synthesized nanomaterials. The Mössbauer spectra of the samples were recorded at room temperature in transmission geometry using 25mCi ⁵⁷Co source in
Rh matrix. The isomer shift (I. S.) values are reported with respect to standard natural iron foil. The hysteresis curves of all the samples were recorded by using a vibrating sample magnetometer (Princeton-150 A) at room temperature.

3. Results and Discussion

The X-ray diffraction patterns of the prepared samples show the presence of cubic spinel phase. A small trace of ZnO phase also appears in the prepared samples (Figure 1 and 2). The average crystallite size was estimated by using the Scherrer’s formula [15]. The crystallite size varies from 9±1 to 29±1 nm and 9±1 to 40±2 nm as the sintering temperature varies from 300 to 600°C for the sintering time of 2 and 3 h respectively (Figure 3). Figure 4 shows the TEM micrograph of the sample ZF3-300. The average particle size has a value of 24±10 nm for this system which may be due to agglomeration of several crystallites.

![Figure 1. XRD pattern of the samples sintered for 2 h at various temperatures.](image1)

![Figure 2. XRD pattern of the samples sintered for 3 h at various temperatures.](image2)

![Figure 3. Average crystallite size of the samples as a function of sintering temperature.](image3)

![Figure 4. Transmission electron micrograph of the sample ZF3-300.](image4)

Figure 5 and 6 show the room temperature (RT) Mössbauer spectra of the samples. All the spectra were fitted by a doublet and the hyperfine parameters are shown in Table 1. The values of I. S. are of the order of 0.40 mm/s and are large as compared to the previous studies [11,13]. The values of I. S. in the samples are attributed to the presence of Fe^{3+} state in the samples. The large values of quadrupole splitting (Q. S. ~ 0.40 mm/s) for these systems compared to the bulk value of 0.35 mm/s [9] may be attributed to the cation inversion in these samples [16]. The line-width (L. W.) of the samples changes from 0.32 to 0.37 mm/s. The change in L. W. may be attributed to the change of surface strain or domain pinning [17]. Due to the small crystallite size and large surface area, Mössbauer nuclides
sitting at the surface are not bonded that strongly, causing a decrease in the recoil free fraction, and therefore the area under the curve (Figure 7) is small for the smaller size particles [11, 13].

Table 1: RT Mössbauer hyperfine parameters of the samples

| Thermal Treatment | Mössbauer Hyperfine Parameters |
|-------------------|-------------------------------|
| Sintering Time (h) | I.S. (mm/s) | Q. S. (mm/s) | L.W. (mm/s) |
|                   | ±0.01 | ±0.01 | ±0.01 |
| 2                  |       |       |       |
| 300                | 0.39  | 0.42  | 0.32  |
| 400                | 0.39  | 0.41  | 0.32  |
| 500                | 0.40  | 0.40  | 0.31  |
| 600                | 0.41  | 0.40  | 0.32  |
| 3                  |       |       |       |
| 300                | 0.40  | 0.43  | 0.37  |
| 400                | 0.40  | 0.40  | 0.36  |
| 500                | 0.42  | 0.40  | 0.33  |
| 600                | 0.40  | 0.40  | 0.35  |

Figure 5. RT Mössbauer spectra of the samples sintered for 2 h at various temperatures

Figure 6. RT Mössbauer spectra of the samples sintered for 3 h at various temperatures.

Figure 7. Absorption area versus sintering temperature for the samples.

Figure 8. Hysteresis curve of the samples.

The Mössbauer hyperfine parameters remain almost constant within experimental error with respect to the various heat treatments for all the samples. To understand the magnetic behaviour of our samples
we performed the magnetization measurements at room temperature (Figure 8). The hysteresis curve of the samples ZF2-300 and ZF3-400 show almost zero value of coercivity and retentivity, showing the presence of superparamagnetism at room temperature in these samples (Figure 8: inset). Rest of the samples show the paramagnetic behaviour at room temperature. The crystallite size of the samples ZF2-300 and ZF3-300 are comparable ~ 9 nm and the Mössbauer spectrum contains a doublet in both the samples. But the hysteresis curve shows the presence of superparamagnetism in the sample ZF2-300 and paramagnetism in the sample ZF3-300. This controversy is under investigation.

4. Conclusion

The XRD of the synthesized samples show the presence of cubic spinel phase; however ZnO appears as an impurity phase in the samples. The crystallite size increases as the sintering time and temperature increases. The Mössbauer spectra of the samples show the presence of doublet, which is attributed to superparamagnetic/paramagnetic nature of the samples as determined from the VSM measurements. The values of I,.S. are the particulars of Fe$^{3+}$ state in nanostructured zinc ferrite. The Q. S. shows the attributes of cation inversion in the synthesized samples. Further, no regular trend in the magnetization was found with the particle size. The peculiar behavior of the samples ZF2-300 and ZF3-300 are under investigation.

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