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Preparation, characterisation and magnetic studies on nanocrystalline $Co_{0.4}\,Zn_{0.6}Fe_2O_4$

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Abstract: *Nanocrystalline $Co_{0.4}\,Zn_{0.6}Fe_2O_4$ have been synthesized by co-precipitation method. Nanocrystalline ferrites with average crystallite size of 2.7-39.9 nm were obtained by sintering the samples between 393K and 1173K. FTIR show that the spinel ferrites prepared by co-precipitation method retain some hydroxyl groups and is not removed completely by sintering below 873K. FC/ZFC measurements show that the ferrite samples are superparamagnetic having a blocking temperature around 78K. Magnetization at 1 Tesla of Zn=0.6 samples increases with increasing average crystallite size only upto 14 nm and for samples with crystallite size > 14nm, magnetization decreases with increasing crystallite size due to change in cation distribution.*

Key words: *Nanocrystalline, spinel ferrite, crystallite size, Superparamagnetic, Magnetization, cation distribution*

I. Introduction

Spinels are compounds with space group O_h^7 (*Fd3m*) and general formula AB_2X_4 where A and B are cations and X is the anion. The spinel structure consists of FCC closed packed array of 32 anions in which 1/8th of the tetrahedral and 1/2 the octahedral interstices are occupied by metal ions [1].

In cubic ferrites, the magnetic ions can occupy both tetrahedral (A) and octahedral (B) sites of the spinel lattice which allows various cation distributions and this makes the ferrites useful and interesting as application materials. The magnetic exchange integrals (J_{AB}, J_{BB} and J_{AA}) are generally negative with the antiferromagnetic interaction A-O-B stronger than B-B and A-A interactions [2]. When a non magnetic ion is introduced in the lattice a competition between ferromagnetic and antiferromagnetic interactions leads to spin glass or cluster glass behaviour [3-6].

Nanocrystalline ferrite materials are very useful because of their unique relationship between magnetic properties and particle size e.g. reduced magnetization [7], enhanced coercivity [8], superparamagnetism [9].

In many electronic and magnetic applications it is important to fabricate a ceramic material of desirable microstructure with small particle size. Various preparation methods have been developed to obtaining nanosize ferrite particles like co-precipitation [10], solgel [11], hydrothermal [12], microemulson [13].

The present work aims at synthesizing nanocrystalline $Co_{0.4}\,Zn_{0.6}Fe_2O_4$ samples by co-precipitation method followed by sintering, characterize them by X-ray diffraction (XRD), Fourier Transformed infrared spectroscopy (FTIR), Transmission electron microscope (TEM), and study the effect of particle size on their magnetic behaviour.

II. Experimental

The $Co_{0.4}\,Zn_{0.6}Fe_2O_4$ nanocrystalline samples were prepared by co-precipitation method. A mixed solution of stoichiometric amounts of $CoCl_2$, $ZnSO_4$ and $Fe(NO_3)_3$ was prepared. This mixed solution was added dropwise from a burette into NH_4OH solution, maintaining the pH at ~8. The pH of the solution was kept constant by adding dilute NH_4OH from another burette. The resultant mixture was boiled at 353K for 30 minutes and then allowed to settle. The precipitate was filtered, washed with de-ionized water several times and then dried in vacuum (0.05 Torr) at room temperature. The dried precipitate was then sintered at various temperatures (393K, 573K, 673K, 773K, 873K, 973K, and 1173K) for 12 hrs.

X-ray diffraction analyses of all the samples were carried out with a Phillips X-ray diffraction unit (model PM 1710) using CoK_α (λ=1.79 Å) and CuK_α (λ=1.5418Å) radiation with a Ni filter. The crystallite size of the nanocrystalline samples were determined from X-ray line broadening analyses applying Scherrer formula [14].

Cation distribution of the nanocrystalline samples was determined from X-ray diffraction data by comparison of observed and theoretically calculated intensity ratios of various reflections[15].

Microstructural analysis of the $Co_{0.4}Zn_{0.6}Fe_2O_4$ sample was carried out using a transmission electron microscope (TEM) (Model JEM 200 CX) operating at a voltage of 120 kV. Particle size of the sample was determined from the TEM micrograph.

FTIR spectra of all the samples were recorded in KBr medium in the range 400-4000cm^{-1} with a Thermo Nicolet Nexus FTIR (model 870).

The magnetic measurements were carried out using a vibrating sample magnetometer (VSM) between 7K and 303K.

III. Results And Discussion

The XRD patterns in Fig.1 show that all the $Co_{0.4}Zn_{0.6}Fe_2O_4$ samples sintered at temperatures between 393 K and 1173 K are single phase spinel oxides. The figure however, show that the lines in the XRD patterns of samples sintered below 773 K, are not very sharp as is expected for nanocrystalline samples. The average crystallite size of these samples were found to be in the range of 2.7nm to 39.9 nm. The lattice parameter and crystallite size values of these samples are shown in Table 1. The results in the table show that there is no change in the lattice parameter with change in the sintering temperature i.e. crystallite size. These results indicate that the $Co_{0.4}Zn_{0.6}Fe_2O_4$ nanocrystalline samples prepared by co-precipitation method followed by sintering upto 1173 K are nanocrystalline spinel ferrites.

Fig. 2 shows the TEM picture of the $Co_{0.4}Zn_{0.6}Fe_2O_4$ sample sintered at 573K. The picture shows the presence of agglomerated particles. The average particle size of this sample determined from the TEM pictures, is 5.6 nm which is larger than the crystallite size determined from the XRD pattern as has also been found in other ferrites [16].

To further confirm the formation of the spinel phase, FTIR of the samples was recorded. Fig 3 shows the FTIR spectra of the ferrite samples sintered at various temperatures. The presence of bands in the 400-550cm^{-1} range in all the spectra, confirm the formation of the spinel phase. The FTIR spectra of the samples sintered upto 873 K however show some additional absorption bands around 3400cm^{-1} and 1620 cm^{-1} respectively. A broad band appearing near 3400 cm^{-1}can be assigned to the symmetric stretching mode of vibration of –OH and the band near 1620 cm^{-1} can be assigned to the bending mode of –OH as has been reported earlier [17].

The temperature dependence of dc magnetization in 0.1 T applied field is shown in Fig. 4 shows that for the 573K sintered samples ZFC magnetization, $M_{ZFC,}$ gradually increases with increasing temperature from 7K and then a broad maxima appears, followed by decrease of M_{ZFC}. On heating the samples, the FC magnetization curves of both the samples do not follow the ZFC curve below the temperature of maxima in the ZFC plots. These results clearly show that the samples are superparamagnetic having blocking temperature around 78K.

Fig. 5 show the magnetization vs applied field (upto 1T) plots of all the $Co_{0.4}Zn_{0.6}Fe_2O_4$ samples. Figure 5 show that for the CZ6 samples sintered above 873K, with increasing magnetic field, magnetization initially increases followed by very little change, implying magnetization saturation occurs below 1 Tesla. The samples sintered below 873 K however show a regular increase in magnetization with no tendency of magnetization saturation. Such behaviour is usually expected in superparamagnetic samples. Thus it appears that the samples sintered below 873K are probably superparamagnetic as has been observed in $Co_{0.2}Zn_{0.8}Fe_2O_4$ [18]. This possibility is also supported by the very small average crystallite size of these samples (Table 1). Fig. 5 shows that the M_{1T} values of the CZ6 samples with crystallite size ≤ 14nm increase with increasing crystallite size. However, the M_{1T} values of the CZ6 samples with crystallite size > 14 nm, decrease with increasing crystallite size. Increase in magnetization value with increasing sintering temperature i.e. crystallite size, is expected but the trend shown in CZ6 samples with crystallite size > 14 nm is rather unusual. Similar results were however reported for $CuFe_2O_4$ [19] and $ZnFe_2O_4$ [20] samples, where saturation magnetization was found to decrease with increasing particle size. Jiang et al [19] attributed this unusual change mainly due to a drastic change in cation distribution, and also due to spin canting. Recent studies on nanocrystalline cobalt ferrite have shown that net moment increases with increasing particle size [21]. This trend is followed in the present results on going from CZ639 to CZ687. But in CZ697 and CZ6117, the crystallite size is larger but the net moment is smaller. This is only possible if the net moment due to the interactions between Fe_A and Fe_B in the CZ6 samples become smaller. As mentioned earlier the magnetic interactions in spinel ferrites are Fe_A-O-Fe_B > Fe_B-Fe_B > Fe_A-Fe_A and hence smaller net magnetic moment will be expected when the amount of either Fe_A or Fe_B is reduced in the ferrite.

Earlier studies on spinel ferrites have shown that the cation distribution in the nanocrystalline phase is usually different from that in the bulk phase and this can lead to change in the magnetic interactions and net magnetic moment of the ferrite [22]. Thus to investigate the cause of decrease in the net magnetic moment of the CZ samples, the cation distribution of these samples were determined. Table 2 shows that the cation distribution in cobalt zinc ferrite, changes with change in particle size and that in the samples with particle size > 14 nm, Fe^{3+} on the tetrahedral site is quite small. Similar results have been shown by Dey et al [23] in $Co_{0.2}Zn_{0.8}Fe_2O_4$. Hence it appears that smaller magnetization values in the ferrites with larger particle size, is due to change in cation distribution. Site preference energy calculations, have shown that Zn^{2+} has strong tendency to occupy tetrahedral sites [24], but Table 2 shows that in the samples sintered below 873K, considerable amount of Zn^{2+} is on the octahedral site of the spinel lattice. Earlier Jeyadevan et al [25] had shown that in manganese zinc ferrite, prepared by co-precipitation method and sintered at 373K, non magnetic zinc ions occupy tetrahedral and octahedral sites randomly. Thus it appears that in the present studies, change in magnetization of the samples sintered at different temperatures is due to random distribution of the non magnetic Zn^{2+} ion on both tetrahedral and octahedral sites of the spinel lattice and this affects the magnetic properties of the samples. Thus it may be concluded that the anomalous change in magnetization values with change in particle size is mainly due to a change in the distribution of Zn^{2+} on the octahedral and tetrahedral sites of the spinel lattice.

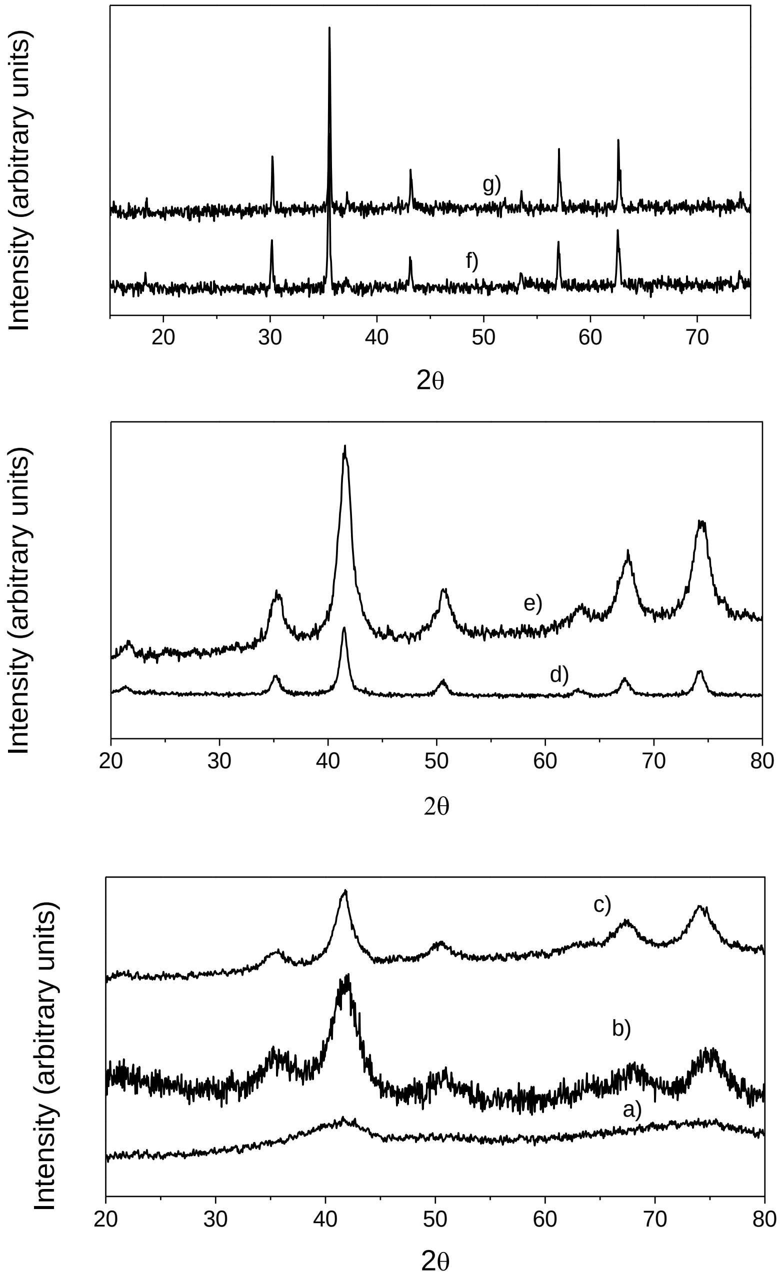
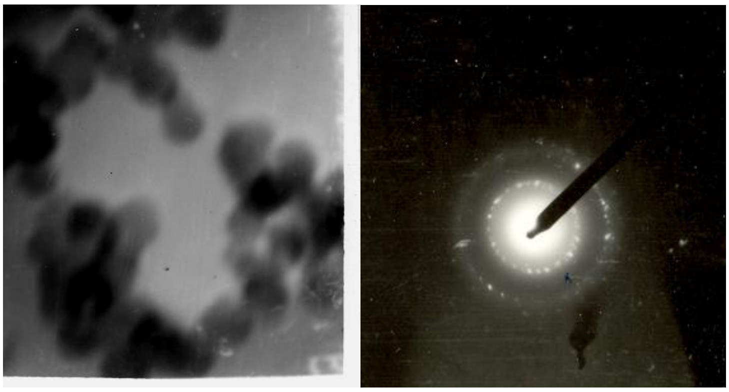


Fig. 1 A. XRD patterns of $Co_{0.4}Zn_{0.6}Fe_2O_4$ samples sintered at a) 393K, b) 573K, c) 673K, d) 773K, e) 873K, f) 973K and g) 1173K.



1 cm = 14 nm

Fig. 2. TEM picture and electron diffraction pattern of $Co_{0.4}Zn_{0.6}Fe_2O_4$ sample sintered at 573K

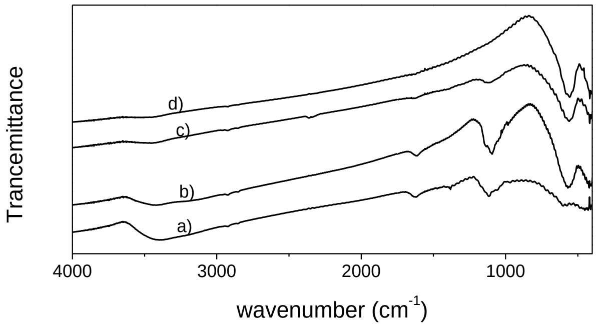


Fig. 3 FTIR spectra of $Co_{0.4}Zn_{0.6}Fe_2O_4$ samples sintered at a) 393K, b) 773K, c) 873K and d) 973K

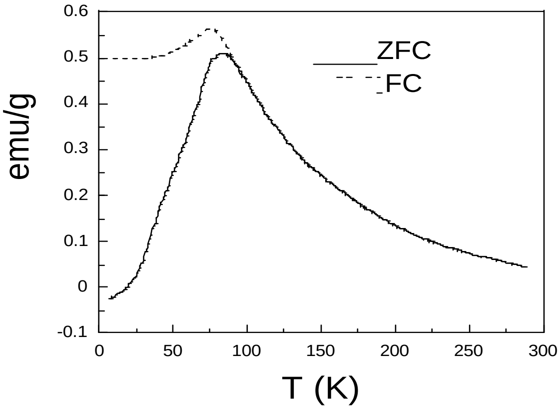


Fig. 4. Zero field cooled (ZFC) and field cooled (FC) magnetization plots $Co_{0.4}Zn_{0.6}Fe_2O_4$ sample sintered at 573K

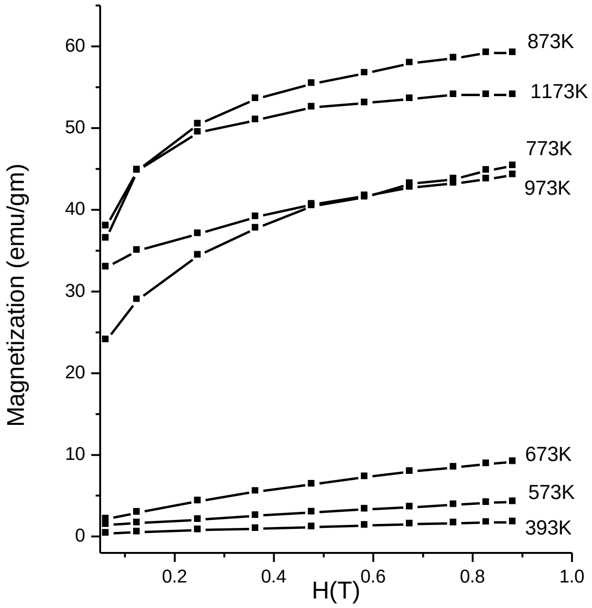


Fig.5 Variation of magnetization with the applied magnetic field of $Co_{0.4}Zn_{0.6}Fe_2O_4$ sintered samples.

TABLE

Table 1: Code name, chemical composition, sintering temperature, lattice parameter and crystallite size of $Co_{0.4}Zn_{0.6}Fe_2O_4$ samples.

Code names	Sintering temperature(K)	Lattice parameter (Å)	Crystallite size (nm)
CZ639	393	8.42	2.7
CZ657	573	8.42	3.4
CZ667	673	8.41	5.8
CZ677	773	8.41	7.1
CZ687	873	8.41	14.2
CZ697	973	8.41	37.9
CZ6117	1173	8.42	39.9

Table 2 Code name, and cation distribution of nanocrystalline $Co_{0.4}Zn_{0.6}Fe_2O_4$ samples

Code name of the samples	Cation distribution
CZ677	$Co_{0.208}Zn_{0.240}Fe_{0.552}[Co_{0.192}Zn_{0.360}Fe_{1.448}]O_4$
CZ687	$Co_{0.340}Zn_{0.270}Fe_{0.390}[Co_{0.060}Zn_{0.330}Fe_{1.610}]O_4$
CZ697	$Co_{0.192}Zn_{0.530}Fe_{0.278}[Co_{0.208}Zn_{0.070}Fe_{1.722}]O_4$
CZ6117	$Co_{0.162}Zn_{0.550}Fe_{0.288}[Co_{0.238}Zn_{0.050}Fe_{1.712}]O_4$

IV. Conclusion

From these results it may be concluded that nanocrystalline $Co_{0.4}$ $Zn_{0.6}Fe_2O_4$ ferrite samples prepared by co- precipitation method and sintered below 873K are superparamagnetic in nature and show a blocking temperature in the ZFC/FC plots. In the $Co_{0.4}$ $Zn_{0.6}Fe_2O_4$ nanocrystalline samples having very small particle size, Zn^{2+} is distributed between the octahedral and tetrahedral sites of the spinel lattice. With change in the crystallite size however, cation distribution of the spinel ferrite changes resulting in an anomalous change in magnetization.

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