Synthesis, characterisation and magnetic studies of $Co_{0.4}Zn_{0.4-x}Cu_xFe_2O_4$ Nanoparticles

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Abstract- Nanocrystalline $Co_{0.4}Zn_{0.4-x}Cu_xFe_2O_4$ have been synthesised by the co-precipitation method. XRD shows that the spinel ferrite is formed. Nanoparticles with average particle size of 10–100 nm were obtained by sintering the samples between 393 and 1173 K. FTIR show that spinel ferrites prepared by precipitation method retain some hydroxyl groups, which are not removed completely by sintering at temperatures <873 K. Saturation magnetization of the samples increase with increasing average particle size upto 11 nm and for samples with particle size >11 nm, the saturation magnetization decreases with increasing particle size. This is due to a change in cation distribution with change in particle size.
Key words- Co-Zn-Cu Ferrites, Nanoparticles, Magnetic properties

INTRODUCTION

Among the most widely used electromagnetic materials over a wide range of frequency, ferrites are one most used due to their high performance and low cost [1]. As the performance in the bulk preparations routs leads to limits due to their higher electrical conductivity and domain wall resonance, the ferrite research has been shifted towards developing these materials in nanometric scale [2,3]. The technological advances in electronics industry demands more compact cores for work at higher frequencies [4]. However, one way to solve this problem is by synthesizing nanoferrites before compacting them for sintering. The domain wall resonance can be avoided by decreasing the size of the magnetic particles than the critical size. Thus the material can work at higher frequencies. Nanocrystalline materials are showing great promise in industry [1,2] and technology. This is mainly because they have some unique properties which are not shown by the bulk crystalline materials [3–5]. In ferrites, the magnetic ions occupy the tetrahedral (A) and octahedral (B) sites of the spinel lattice and the exchange integrals (JAB, JBB, and JAA) are generally negative with the antiferromagnetic interaction A–B stronger than B–B and A–A

interactions [6]. When disorder is introduced in the lattice through dilution by non-magnetic ions, a competition between ferromagnetic and antiferromagnetic interactions leads to spin glass or cluster glass behaviour [7–10]. Nanoferrites can be produced by a number of ways such as coprecipitation of hydroxide [5], sol-gel method [6], hydrothermal[7], micro emulsion method and mechano synthesis approach of ball milling [8] etc. It is not sure that whether the different methods produce the same microstructure but this paper reports the results of coprecipitation and sol-gel method as these methods provide good control over the particle size and are less time consuming. Synthesizing nanocrystalline and to discuss the results of structural and their magnetic behavior of this material at nano scale.

EXPERIMENTAL

$Co_{0.4}Zn_{0.4-x}Cu_xFe_2O_4$ nanoferrite was synthesized by coprecipitation method by taking the high purity starting material, CoCl2, ZnSO4, CuSO4.5H2O and Fe(NO3)3 salts for cationic solution and the sodium hydroxide solution as the base. The heated NaOH solution is poured into the cationic solution in a thin flow while maintaining the pH at 8 and continuing the stirring at 600 rpm and heating at 100°C till the precipitation occurs. The

precipitate was washed and filtered repeatedly before drying and this resulted in very fine particles which were sintered at various temperatures ranging from 400 to 1173 K for 12 Hrs.

The powdered samples were then subjected to characterisation. X-ray diffraction patterns were taken on a Phillips X'pert diffraction using Co Kα radiation with Ni filter. Magnetization measurements were made on a Vibrating Sample Magnetometer at room temperature using a field up to 10 kOe. Magnetisation measurements were made on a Vibrating Sample Magnetometer at room temperature using a field up to 10 kOe. FTIR spectra of all the samples were recorded in KBr medium in the range 400–4000 cm-1 with a Thermo Nicolet Nexus FTIR (model 870).

RESULTS AND DISCUSSION

The XRD patterns in Fig. 1 show that all the samples are single phase spinel oxides. The lines in the XRD patterns of samples sintered at temperatures ≤ 773 K, are not very sharp as is expected for nanocrystalline materials. The average crystallite sizes of these samples were found to be less than 15 nm as shown in (Table 1). These results indicate that the $Co_{0.4}Zn_{0.4-x}Cu_xFe_2O_4$ samples prepared by precipitation method followed by sintering are nanocrystalline spinel ferrites. Fig. 2 shows the FTIR spectra of the ferrite samples. The presence of bands in the range (400–550 cm^{-1}) in the spectra, confirm the formation of the spinel phase. Some additional absorption bands around 3400–3200 cm^{-1} and 1120 cm^{-1}, respectively are also present in the FTIR spectra of some of the samples (Fig. 2a, b and c). These bands correspond to the stretching and bending modes of –OH group. From these results it appears that hydroxyl groups are retained in the samples during preparation of the spinel ferrites by precipitation method and is not completely removed even after sintering at 873 K.
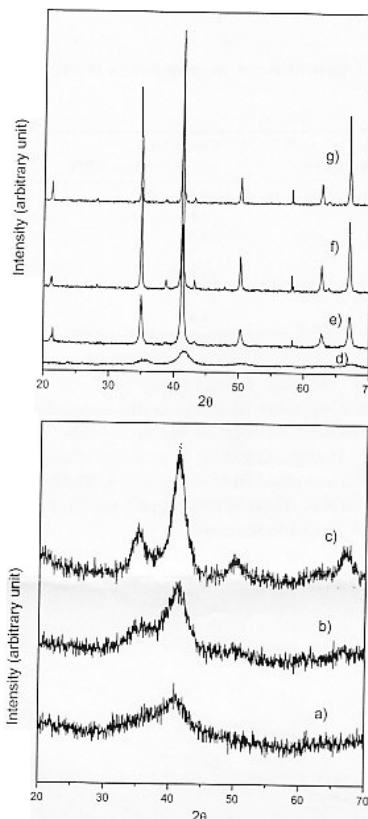

Fig.1- XRD Patterns sintered at (a) 395 (b) 573 (c) 673 (d) 773 (e) 873 (f) 973 and (g) 1173 K

The FTIR spectra in Fig. 2c however show that the amount of hydroxyl in the 873 K sintered sample is much less than in the samples sintered below this temperature, suggesting that hydroxyl is gradually removed as the sintering temperature is increased. The bands around 3400–3200 and 1120 cm^{-1} are absent in the spectra of the sample sintered at 973 K, (Fig. 2) implying that hydroxyl is completely removed when the sample is sintered at temperatures ≥ 973 K. The results from XRD (Fig. 1) show that there is a sudden change in crystallinity of the samples when the sintering temperature is increased from 873 to 973 K. The crystallite size also shows a sudden increase from 13.5 to 35 nm (Table 1). These results suggest that the presence of hydroxyl in the sample partially inhibits crystallization and particle growth.

Code names	Sintering temperature (K)	Crystalline size (nm) from XRD
CZCuF12	395	1.58
CZCuF30	573	3.2
CZCuF40	673	5.50
CZCuF50	773	5.75
CZCuF60	873	13.50
CZCuF70	973	35.27
CZCuF90	1173	45.87

Earlier studies on these samples had shown that the samples with particle size ≤ 13 nm i.e. samples sintered at temperatures≤873K,are superparamagnetic while samples with particle size ≥15 nm i.e. samples sintered at temperature ≥973 K show clustering [23].
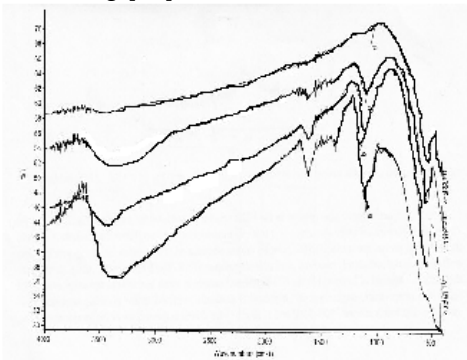

Fig. 2-FTIR Spectra of Co-Zn-Cu ferrite samples sintered at different temperatures.

In order to ascertain if the magnetic behavior of these samples are influenced by the presence of hydroxyl in the samples, magnetization measurements were carried out at room temperature (303 K). The results of magnetization measurements (M) versus applied field (H) (Fig. 5) show that saturation is not reached upto a field of 1 T. This is expected as it has been shown earlier that the magnitude of the magnetic field required to reach saturation magnetisation depends on the size of the particles [24]. Fig. 4 shows that for the smaller particles, M versus H plots are almost linear showing no indication of magnetisation saturation as is expected in a superparamagnetic material. The plot of the sample having an average particle size of 10 nm is quite irregular implying that there is magnetic inhomogeneity in this sample. For the samples with average particle size ≥11 nm, magnetization values at 1 T (M1 T) show an increase with increasing particle size as has been also observed in other nanocrystalline spinel ferrites and has been attributed to spin canting [25]. Spin canting in nano crystalline ferrites has been explained by two mechanisms, one is the surface effect [25–28] and the other is the finite size effect [29,30]. Fig. 5 shows that the M1 T values of the $Co_{0.4}Zn_{0.4-x}Cu_xFe_2O_4$ samples with particle size ≥15 nm, decrease with increasing particle size. Increase in magnetization value with increasing sintering temperature i.e. particle size, is expected but the trend shown in samples with particle size ≥15 nm is rather unusual. Similar results were however observed in the studies on nanocrystalline $CuFe2O4$ and $ZnFe2O4$ [8, 31], where saturation magnetization was found to decrease with increasing particle size.
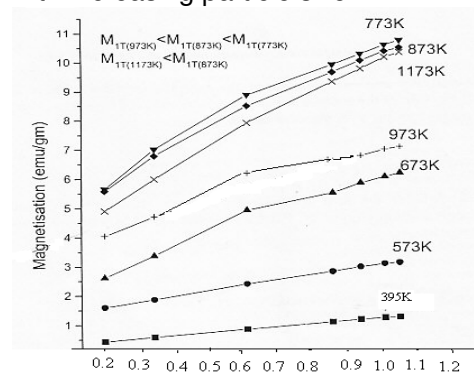

Fig.3-Variation of magnetization with the applied magnetic field of Co-Zn-Cu ferrite sintered at different temperatures. Jiang et al. [31] attributed this unusual change in magnetization to spin canting and a drastic change in cation distribution. However, they suggested that the

main contribution for decrease in magnetization with increasing particle size is due to a change in the cation distribution. In the present studies FTIR results have shown that hydroxyl is absent in the samples sintered above 600°C. Hence, it may appear that the decrease in the magnitude of M1 T is related to the removal of hydroxyl from the samples. However, low temperature magnetization studies by Dey et al. [23], have shown that the cation distribution in $Co_{0.4}Zn_{0.4-x}Cu_xFe_2O_4$ changes with change in particle size and that in the samples with particle size ≥15 nm Fe3þ on the tetrahedral site is quite small. Hence, it appears that smaller magnetization values in the ferrites with larger particle size, is due to change in cation distribution and not due to removal of hydroxyl from the samples.

CONCLUSION

From these results it may be concluded that nanocrystalline $Co_{0.4}Zn_{0.4-x}Cu_xFe_2O_4$ samples can be prepared by precipitation method followed by sintering at 393 K. Samples sintered below 973 K retain some of the hydroxyl formed during the preparation of the samples by precipitation method. On removal of the hydroxyl, the crystallinity and particle size of the samples increase without any change in their morphology. With increase in the particle size, cation distribution of $Co_{0.4}Zn_{0.4-x}Cu_xFe_2O_4$ changes resulting in a decrease in magnetization with increase in particle size.

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