



Magnetic Properties of Zn Substituted Cobalt Ferrite

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Abstract: The magnetic and structural properties of Zn substituted cobalt ferrite prepared by solid state reaction were studied. All the compositions in the series $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (CZF series) where $x = 0.0, 0.1, 0.2, 0.3, 0.4,$ and 0.5 were synthesized by conventional solid state method. Structural analysis confirmed the formation of spinel phase with no secondary phases or impurities formed. A linear variation of lattice parameters indicated complete solid solution formation. The saturation magnetization increased from 78 emu/gm to a maximum value of 92 emu/gm for $x = 0.2$. The observed magnetic properties changes could be explained based on the cationic distribution of Zn ions in spinel lattice.

Introduction:

Research on magnetic materials, especially spinel ferrites has been fairly active in the last several years because of the wide range of potential applications including digital recording heads, sensors, transformers, telecommunications and computers etc.^{1,2} Magnetic properties of ferrites have been widely studied because of their relevance to magnetic recording, biomedical applications, etc. Among all magnetic oxides, magnetite (Fe_3O_4) presents the most interesting properties because of the presence of iron cations in two valence states, Fe^{2+} and Fe^{3+} in the inverse spinel structure. It has been reported that the magnetic properties of the spinel type ferrites can be tuned by effectively substituting various metal ions in the ferrite lattice. Substitution of small amount of other ions can lead to cation redistribution in the octahedral and tetrahedral sites of the spinel structure thereby causing changes in the saturation magnetization and coercivity of the materials. The magnetic properties of substituted cobalt ferrite have been studied in details in order to explore its applications in high density storage, sensors and high frequency applications.^{3,4,5,6} Spinel structure generally represented as AB_2O_4 where A represents the divalent ion and B represents the trivalent ion. Cobalt ferrite possesses inverse spinel structure and it has been reported that the trivalent ion Fe^{3+} is distributed equally in the tetrahedral and octahedral site.² However this type of cation distribution is very sensitive towards the method of synthesis, annealing temperature etc and finding out exact cation distribution for a specific composition requires support from multiple techniques such as IR, XPS and Mossbauer spectroscopy. The substitution of different cations such as Zn, Ga, Cd, etc has been carried out in cobalt ferrite and it is possible to carry out the substitution for both Co or Fe in CoFe_2O_4 .^{7,8,9}

One of the promising applications of cobalt ferrite is in the field of magnetostriction sensor. Cobalt ferrite because of its anisotropic nature and high spin orbit coupling of Co^{2+} ions, exhibits highest magnetostriction amongst oxide based materials. Cobalt ferrite has been reported to exhibit magnetostrictive strains between 200 to 300 ppm depending on the preparation method, sintering condition and additives.^{10, 11, 12} Recently Nalla *et al.* have studied magnetoelastic properties of cobalt ferrite in which Zn was substituted for Cobalt.¹³ Zn substitution results in dilution of the magnetic lattice although there is a decrease in the

magnetostriction, it was observed that the slope of magnetostriction could be enhanced due to reduction in magnetic anisotropy.

Since Co is mainly responsible for anisotropy in cobalt ferrite, we have carried out direct substitution of non magnetic Zn for Co in cobalt ferrite in order to investigate the effect on magnetic behavior. Zn substitution is likely to affect the cation distribution and thereby significantly alter the magnetic properties.

Experimental:

All the compositions in the series $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (CZF series) where $x = 0.0, 0.1, 0.2, 0.3, 0.4,$ and 0.5 were synthesized by conventional solid state method. Stoichiometric amounts of CoCO_3 , ZnO and Fe_2O_3 were mixed using agate mortar pestle using acetone as a grinding medium. After thorough initial mixing of the starting materials, they were calcined at 1000°C for 24 hours with two intermediate grindings. This was followed by calcination at 1100°C for 72 hours with three intermediate grindings to ensure complete spinel phase formation. The phase purity of the compounds was studied using the X-ray diffraction. The magnetization and coercivity was calculated by using Vibrating Sample Magnetometer (VSM EG&G PAR 4500). The sintering behavior was observed by Thermal Mechanical Analyzer (TMA). The microstructural details were revealed by using Leica Cambridge 440 Scanning Electron Microscope (SEM).

Results and Discussion:

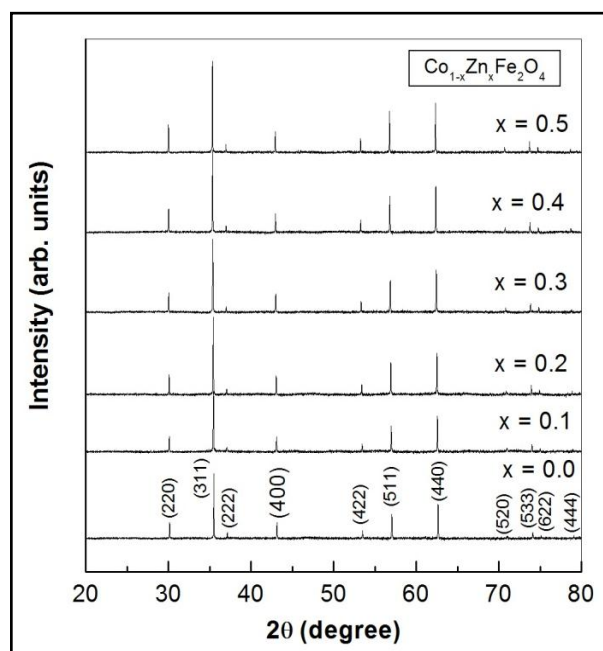


Figure 1. x-ray diffraction patterns of the samples in the series $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$

Figure 1 shows the powder x-ray diffraction patterns for the samples in CZF series. All the composition from $x = 0.0$ to $x = 0.5$ were confirmed to have spinel structure with all the reflections corresponding to the spinel phase and were in agreement with the previous reports (Ref). The simulated x-ray diffraction pattern for cobalt ferrite has been shown in the figure for comparison. No extra reflections were observed in the xrd pattern indicating that the obtained samples are very much pure in phase. The lattice parameter was calculated using the powder cell 2.0 refinement software. ZnFe_2O_4 is higher lattice parameter as compared to CoFe_2O_4 which is attributed to larger ionic radii of Zn^{2+} ions (0.82\AA) as compared to Co^{2+} ions (0.78\AA).¹⁴ Therefore the lattice parameter is expected to increase with increasing Zn content. The variation of lattice parameter with increasing Zn concentration is shown in *figure 2*. Although the lattice parameter increases with increase in the Zn content, it is observed that this rise in lattice parameter is linear and is in agreement with Vegard's law indicating formation of solid solution.

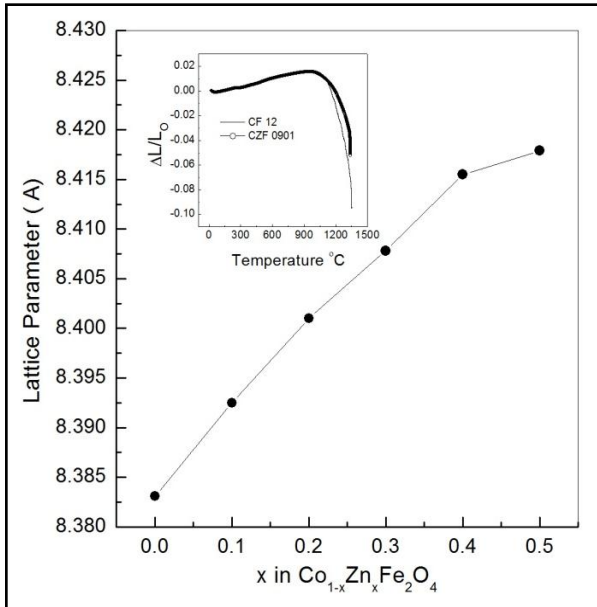


Figure 2. Variation in lattice parameter with Zn content for samples in the series $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$. Inset shows the TMA studies for $x = 0.0$ and 0.1 samples.

The sintering behavior of the samples with $x = 0$ and 0.1 was studied using a thermal mechanical analyzer. TMA provides measurement of penetration, expansion, contraction and extension of material as a function of temperature. The samples were palletized into disk shaped pellets by using 2 % PVA as a binder. The powder samples were pressed uniaxially in the form of 10 mm diameter green pellets and were slowly sintered with a heating rate of $10^\circ\text{C}/\text{min}$ at 1350°C . It was observed that that the effective sintering starts above 1000°C and the sintering is not complete till a maximum temperature of 1350°C . In order to ensure complete and effective sintering the samples were sintered at 1450°C and studied for their micro-structural features. In order to use these materials for any applications it is very important to understand the micro-structural feature since microstructure has a strong influence on the magnetic properties.

It was observed that till the measurement temperature the densification of the samples is not complete which is in agreement with the density measurements reported below.

3.2.1 Determination of Density:

Table: 6 Density of the sample in CZF and CNF series.

X in $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$	X-ray density (g/cm ³)	Experimental Density	Experimental Percent Density (% D)	Lattice parameter (Å)
X = 0.0	5.223	4.848	92	8.3831
X = 0.1	5.286	4.609	87	8.3925
X = 0.2	5.2848	4.710	89	8.401
X = 0.3	5.286	4.767	90	8.4078
X = 0.4	5.862	4.710	89	8.4155
X = 0.5	5.2960	4.767	90	8.4179

It can be observed from the table 6, that the density obtained is almost 90 to 92%. The theoretical density was considered as 5.27 gm/cc [2]. But the theoretical density obtained is 5.2957 gm/cc [10]. A disc shaped pellet was prepared and its weight was noted. The diameter and height of the disc was measured using vernier caliper. Percentage theoretical density (% D_{th}) calculations were made using the formula:

$$\%D (\text{gm}/\text{cm}^3) = \text{measured density } (D_m) / \text{theoretical density } (D_{th})$$

The theoretical density of CoFe_2O_4 was calculated taking the molecular weight of CoFe_2O_4 to be 234.63 g. Spinel ferrites have eight formula units per unit cell. Therefore, the molecular weight of one cell is $8 \times (234.63) = 1877.04$ g. The volume of a cube of side, length a is a^3 . The volume of a cell is therefore $N \times a^3$ where N is Avogadro's number. The unit cell edge $a_0(\text{\AA})$ of $\text{CoFe}_2\text{O}_4 = 8.38$ therefore $a^3 = 588.48 \text{\AA}^3$.

As $1 \text{\AA}^3 = 10^{-24} \text{cm}^3$, $N \times a^3$ is therefore:

$$[6.023 \times 10^{23}][588.48 \times 10^{-24}] = 354.44 \text{ cm}^3$$

Density = mass/volume = $1877.04/354.44 = 5.2957 \text{ g/cm}^3$

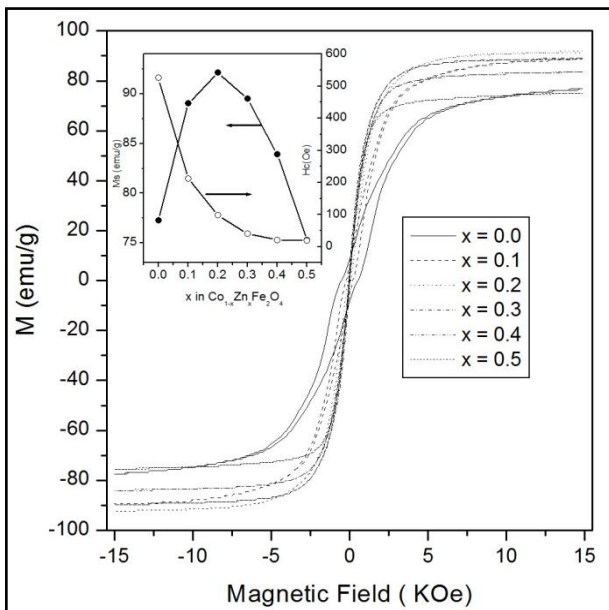


Figure 3. Magnetic hysteresis loops recorded at room temperature for all the compositions in the series $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$. Inset shows variation of coercivity and saturation magnetization with x .

The magnetic field dependence of magnetization (M - H) curves recorded at room temperature for all the compositions is shown in figure 3. The value of saturation magnetization for pure cobalt ferrite was observed to be 77 emu/gm which is in agreement with previous reports¹¹. Continuous rise in the saturation magnetization up to $x = 0.2$ was observed with M_s values of 89 and 92 emu/gm respectively for $x = 0.1$ and 0.2 which subsequently decreased for further Zn doping. The compositions $x = 0.3$ and 0.4 exhibited higher value of saturation magnetization as compared $x = 0.0$ sample. The substitution of non magnetic Zn^{2+} ions has been reported to exhibit similar changes in magnetization in previous literature report and it has been assigned to the site distribution of Zn^{2+} ion in the spinel structure. The site distribution of Zn^{2+} ions in cobalt ferrite lattice has been investigated in detail by Yadav *et al.* and it was confirmed using XPS that all the three ions Fe^{3+} and Zn^{2+} are distributed over the octahedral and tetrahedral sites with Zn^{2+} ions preferentially occupying the octahedral site.¹⁵

Such a behavior can be explained based on the fact that the Zn^{2+} ions in spinel structure have a strong preference for the tetrahedral site. So increasing the Zn content will push the Fe ions present on the tetrahedral site to the octahedral sites. Since Zn^{2+} ions have no net magnetic moment associated with them it will reduce the total moment associated with the A-site. Pushing of Fe ions in the octahedral site leads to an increase in the magnetic moment associated with the B-site. Therefore the net magnetic moment associated with the samples increases because of an overall increase of the sublattice magnetization. This is reflected in the hysteresis curves where the magnetization is high up to $x = 0.4$ as compared with the unsubstituted sample. However at higher concentrations Zn ions may also be forced to occupy the octahedral sites which can result in a decrease of magnetization. The Coercivity of the samples was found to decrease drastically with increasing Zn content which is an indication of decreasing anisotropy of cobalt ferrite with Zn content.

The microstructure of the different compositions in the CZF series is shown in figure. All the micrographs were recorded on fractured surfaces. As can be seen from the micrographs the fractured surface indicated the presence of porosity in agreement with the measured density. The average grain size for all the composition was found to be between 2 to 4 μm .

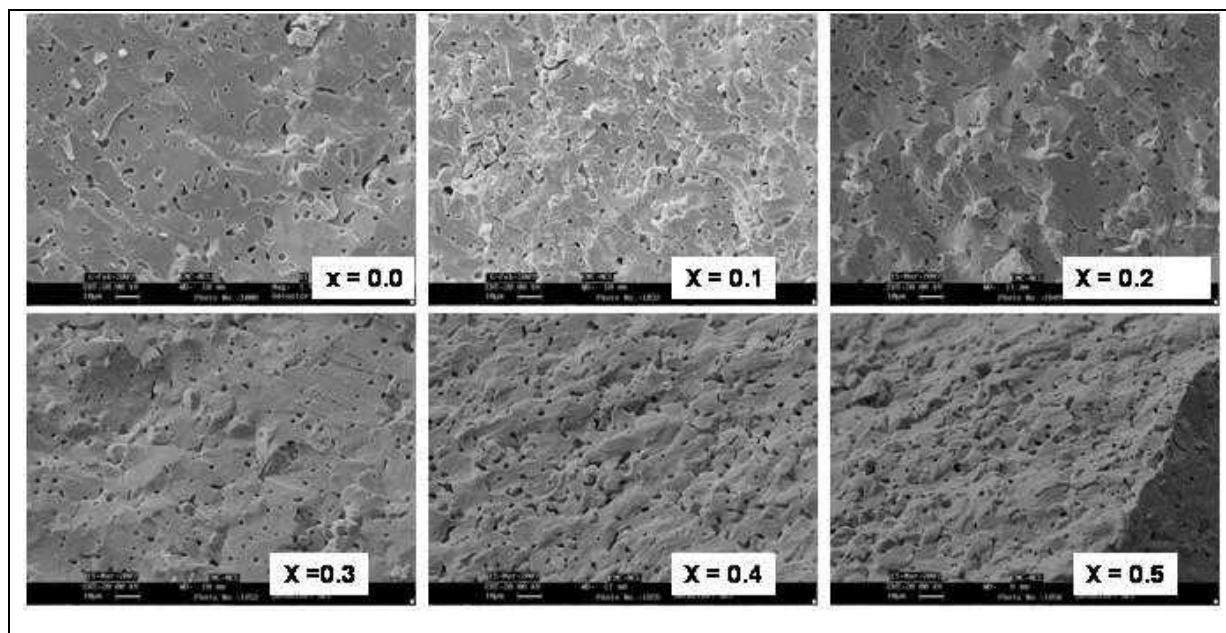


Figure 4. SEM micrographs for all the compositions in the series $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$

Conclusions:

The magnetic and structural properties of Zn substituted cobalt ferrites prepared by solid state reaction were studied. Structural analysis confirmed the formation of spinel phase with impurities formed. A linear variation of lattice parameters indicated complete solid solution formation. The changes in magnetic properties could be explained based on the cationic distribution of Zn ions in spinel lattice. The decreased anisotropy makes these materials promising candidates for exploring magnetostrictive behavior.

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