

Structural and Magnetic Properties of Zinc Substituted CoFe_2O_4 Nanoparticles

T. Joseph¹, D. Pamu²

¹Department of Physics, Noble College, Machilipatnam, Andhra Pradesh, India,

²Indian Institute of Technology Guwahati, Guwahati, Assam, India, Ph: +91 361 25 2721.

Corresponding author: tadiparthijos@gmail.com

Abstract: A Series of Zn doped Cobalt ferrite with formula $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.35, 0.5, 0.65$ and 0.8). The nanoparticles were prepared using reverse co-precipitation method with different Zn concentrations. The XRD patterns showed that the undertaken materials exhibit spinel structure with non-preferential orientation. The structure of the as prepared samples $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ is found to be spinel structure and, which is confirmed using X-ray diffraction analysis. The particle size (11.25 nm to 6.24 nm as x varies from 0.2 to 0.8) and its distribution may be controlled by changing the Zn content in the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ investigated by the XRD and HRSEM. The lattice parameters $a = 8.03609 \text{ \AA}$ ($x = 0.2$) is observed to decrease as Zn concentration is increased to $x = 0.8$, ($a = 8.2233 \text{ \AA}$). The saturation magnetization, which decreased from 58.03 to 10 emu/gm for the increase of Zn content from 0.2 to 0.8 moles at room temperature, appears to be due to pronounced growth of magnetic anisotropy. The values of coercivity decreased from 103.50e to 0.9310e as Zn content increased from 0.02 to 0.8. It is observed that the magnetization remanence ratio has decreased from 0.0826 to 0.00048 at room. The magnetic measurements have been carried out using VSM and Tc measurements. The measurements revealed that the samples are super paramagnetic in nature.

Keywords: CoFe_2O_4 ferrites, XRD; Superparamagnetism, VSM, PFM

1. Introduction

The interesting magnetic properties of spinel ferrites of the general formula AB_2O_4 originated mainly from the magnetic interactions between cations with magnetic moments that are substituted in the tetrahedral (A) and the octahedral (B) sites [1]. This spinel structure can be described as a cubic close – packed anion latticed with 1/8 of the tetrahedral and 1/2 of the octahedral intensities filled by cations. In the absence or a preference of the cations for one coordination site or the other, a random distribution would occur: $\text{A}_{1/3}\text{B}_{2/3}(\text{A}_{2/3}\text{B}_{4/3})\text{O}_4$, where parentheses denote octahedral coordinated cations. In fact, however, specific spinel compounds tend toward either of two limiting cation distributions. One is the normal spinel $\text{A}(\text{BB})\text{X}_4$, the second limiting case is the “Inverse” spinel, $\text{B}(\text{AB})\text{X}_4$. The preference of a given spinel for either the normal of inverse arrangement will be determined by the cations sizes, valences, crystal field stabilization energy and other bonding requirements.

CoFe_2O_4 has an interesting inverse spinel structure with Co^{2+} ions mainly in the B sites and Fe^{3+} ions distributed almost equally between the A and B sites, whereas ZnFe_2O_4 is a normal spinel with all the Fe^{3+} ions in the B sites and all the Zn^{2+} ions in the A sites [2]. Spinel structure allows introduction of different metallic ions, which can change the physical properties considerably [3]. Co – Zn ferrites have a mixed structure that could be used for the energy conversion application using the magnetically induced convection for thermal dissipation. The precipitated particles generally showed single-phase fcc final structure for all compositions of zinc. The magnetic parameters such as Ms, Hc, Mr, Tc and particle size were found to decrease with increase in Zn

substitution. In case of particles with higher zinc concentrations, both ferrimagnetic nano particles and particles exhibiting super paramagnetic behavior were present in CoFe_2O_4 , which has a high coercivity (5400 Oe) and moderate saturation magnetization (~80 emu/g), a remarkable chemical stability and a mechanical hardness, which make it a possible material for high density recording media [4, 5]. An additional advantage for ferrites is that, though the choice of various divalent cations in them, the magnetic properties can be finely tuned and tailored according to practical demands [6].

It is interesting to point out here that recently preparation of cobalt ferrites with varying Zn concentration has been reported. In the present work we report a synthesis, structural and magnetic properties of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.35, 0.5, 0.65$ and 0.8) using a reverse co precipitation method.

2. Results and Discussion

2.1 Structural Properties Of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ Nanoparticles

Qualitative X-ray diffraction measurements were performed to investigate the structure and phase identification of the compounds. The observations from the XRD profiles confirmed the formation of single – phase fcc *spinel structure* for all the samples depicted in Fig. 1. No amorphous phase was detected. The XRD patterns could be completely indexed as (220), (311), (400), (511) and (440) for as prepared samples using JCPDS file No. 22 – 1086, which indicate the formation of required ferrite compounds. The X-ray data of all the samples were analyzed and used to determine the lattice constant, The variation of lattice

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Department of Physics, Government College (A), Rajahmundry, Andhra Pradesh, India

constant and d-spacing as function of Zn composition is shown. It is interesting to note that the lattice parameter decreases linearly with increase of Zn concentration and follows Vegard's law in the entire studied range of composition [7]. The lattice parameter falls within the range of the lattice constants of CoFe_2O_4 and ZnFe_2O_4 . The observed linear variation of the lattice constant is consistent with the earlier reports [8]. As the Zn content increases, the lattice constant decrease from 8.3609 Å to 8.2233 Å, which may be attributed to the reduction of surface tension of the nano crystallite with increase of the particle size. However, earlier authors [9] reported marginal decrease as Zn concentration increases up to $x=0.5$ and explained on the basis of preparation method and state of the sample. The smaller values of the lattice constant for wet samples cannot be explained solely on the basis of rearrangement of cations in the spinel lattice due to different formation conditions. It may be due to the different degrees of crystallinity of wet and annealed wet samples resulting from the difference in the temperature of crystallinity.

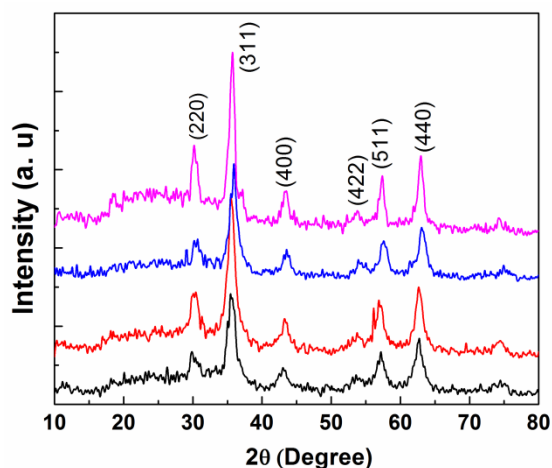


Figure 1: XRD patterns of Co-Zn ferrites nanoparticles.

Table 1: The Structural Data Of Co-Zn Ferrites Nanoparticles.

Variation of Zn	Particle size nm	d-spacing (Å)	Lattice Constant (Å)	D_{XRD} gr/cc
0.2	11.25	2.522	8.3609	5.3603
0.35	9.48	2.5155	8.3432	5.4166
0.5	7.26	2.4999	8.2906	5.5429
0.65	7.05	2.4927	8.2674	5.6123
0.8	6.24	2.4794	8.2233	5.7263

The X-ray densities of samples have been calculated from molecular weight and volume of the unit cell as shown. The density measurements have demonstrated that the density of the sample increases with increasing Zn content in the range from 5.36 gm/cc to 5.72 gm/cc. It is clear from table 3.1 that the increase in molecular weight of the samples overtakes the increase in volume of the unit cell.

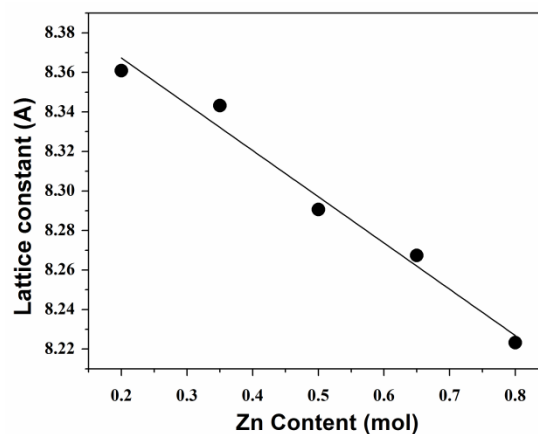


Figure 2: Variation of Lattice constant with Zn content change

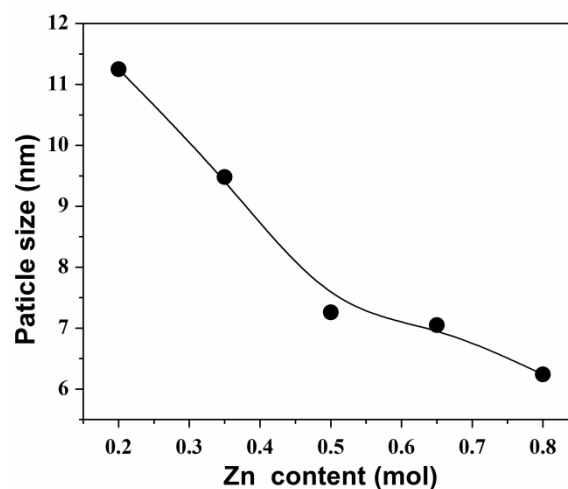


Figure 3: Particle size as function of Zn content change.

The XRD profile peaks were found to be slightly broader in the as prepared samples, because of their particle size effects. The average particle size determined from full width at half maxima (FWHM) of the diffraction line composition has been calculated using the Debye - Scherrer formula for the Co-Zn ferrites to be in the range 11.25 – 6.24 nm as shown in Table.1. The estimated crystallite size values decrease from ~11 nm to ~6 nm as Zn concentration increases from 0.2 to 0.8. Although we have adopted similar synthesis parameters while synthesizing all these compositions we have observed that significant changes takes place in crystallite size. This could be due to changes in sequences of reactions processes between the substituted constituents and nucleation.

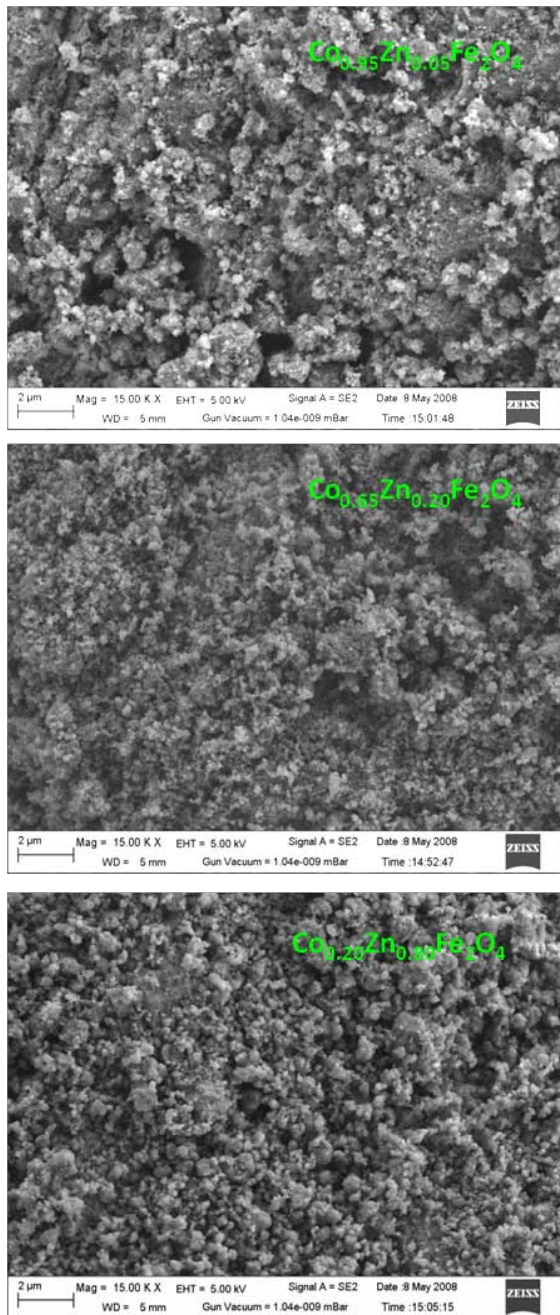


Figure 4. Representation of HRSEM picture of the specified ferrites structures

2.2 Morphological Studies On $Co_{1-x}Zn_xFe_2O_4$ Nanoparticles

The shape and morphology of the fine particles were further examined using a high resolution scanning electron microscope (HRSEM – Hitachi HF 2000) for as prepared samples. The HRSEM analysis for all samples are taken in two magnification i.e 2μm and 200 nm and few images are displayed in Fig.4. The particles can be considered as polycrystalline since the diameter of the particles agrees fairly well with the average crystallite size inferred from the X-ray line broadening analysis and HRSEM images. The HRSEM images show that the smaller particles are nearly spherical and as the particle size increases, they tend to become non-spherical. The size distribution was not determined because of the aggregation of the particles, but particle sizes between 10-25 nm were observed. The particle

size (D_{311}) decreases from 11.25 to 6.24 nm when partial substitution of zinc increases ($x= 0.2$ to 0.8). Direct observation of the lattice image reveals that the particles are approximately spherical in shape and fine particles with higher zinc concentration are agglomerated. In other words, the decrease in particle size led to agglomeration of magnetic fine particles. Because of the small size, single domain particles experience a magnetic moment proportional to their volume and get permanently magnetized. Hence fine particles of size around 10 nm are agglomerated.

2.3 Magnetization Studies Of $Co_{1-x}Zn_xFe_2O_4$ Nanoparticles

The room temperature magnetization measurements have been carried out using a Vibrating Sample Magnetometer (ADE Technologies, USA; Model: 1660 MRS). For each measurement, we used roughly ~25 mg of sample, which gave signal over three orders of the magnitude larger than the magnetic background of the sample holder. We measured magnetization as a function of applied magnetic field for $Co_{1-x}Zn_xFe_2O_4$ products for all the compositions using magnetic field ranging from 0 to 20 kOe at room temperature, Figure 5 shows the room temperature hysteresis loop of the prepared powder samples. The magnetization curves show neither hysteresis nor coercivity. This is characteristic of superparamagnetic behaviour. The M–H loops observed in the present study show that the cation distribution has changed from the normal to the mixed spinal type. Hence some percentage of Fe^{3+} is pushed to the tetrahedral sites, which switches on the A–B super-exchange interaction between Fe^{3+} ions on both sites and gives rise to ferromagnetic ordering. The unsaturated magnetization behavior observed in nanocrystalline zinc ferrite reveals the presence of a superparamagnetic and single domain f the particles [10].

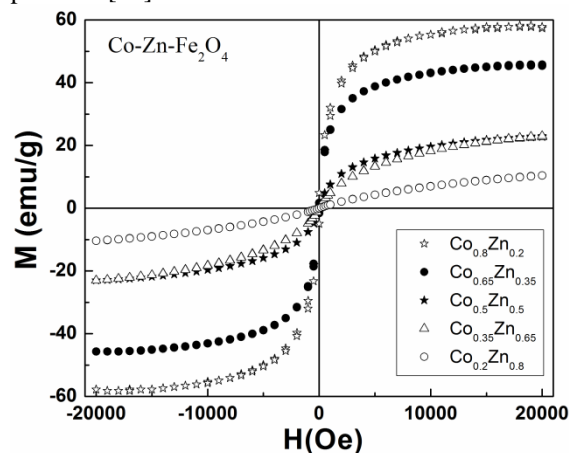


Figure 5 Magnetization versus applied filed for $Co-Zn-Fe_2O_4$ nanoferrites at room temperature.

Table 2: Magnetic Data For The $Co-Zn-Fe_2O_4$ Nanoferrites

Zn content	M_s emu/gm	M_r emu/gm	M_r/M_s	H_c Oe	T_c
0.20	58.03	4.799	0.0826	103.50	292.6
0.35	45.75	1.566	0.0342	40.28	227.7
0.50	23.03	0.029	0.0013	2.971	148.7
0.65	23.00	0.006	0.00026	0.931	80
0.80	10.40	0.005	0.00048	0.405	***

The graph between saturation magnetization (M_s) as the Zn content is shown in Fig. 6. From the graph, M_s decrease linearly as the Zn concentration increases. It can be well fitted by a straight line. The saturation magnetization was found to decrease from 58.03 to 10.40 emu/gm when the concentration of Zinc was increased from 0.2 to 0.8. M_s of Co-Zn ferrites decrease with Zn content due to the strong covalency effects arising from small cationic site dimensions. The saturation magnetization decreases with Zn increased, since the diamagnetic Zn^{2+} ions replace the magnetic Co^{2+} ions at tetrahedral sites due to the prominent inter-sub lattice A-B super-exchange interactions. At room temperature, the value of M_s obtained for our Nanoparticles of $Co_{0.8}Zn_{0.2}Fe_2O_4$ is 58.03 emu/gm and, which is lower than 65 emu/gm for the $CoFe_2O_4$ bulk [28]. But this value is marginally matching with $CoFe_2O_4$ 58.3 emu/gm for 13.8 nm size particle precipitated at 80°C reported by Kim et al [11]. The remanent magnetization M_r with respect to the Zn content change is shown. It is observed that the value of remanent magnetization decreases as a function of the Zn content change. The decrement of the values of remanent magnetization M_r is due to the influence of the cationic stoichiometry and their occupancy, in the specific sites. In the cubic system of the superparamagnetic spinels, the magnetic order is mainly due to a super exchange interaction mechanism that occurs between the metal ions in the A and B sublattices. The substitution of non-magnetic ions such as Zn, which has a preferential A site occupancy, results in the reduction of the exchange interaction between A and B sites. In addition, formation of a dead layer on the surface, existence of random canting of particle surface spins, non saturation effects due to random distribution of particle size, deviation from the normal cations distribution etc., also result in the reduction of magnetic properties of nanosized particle.

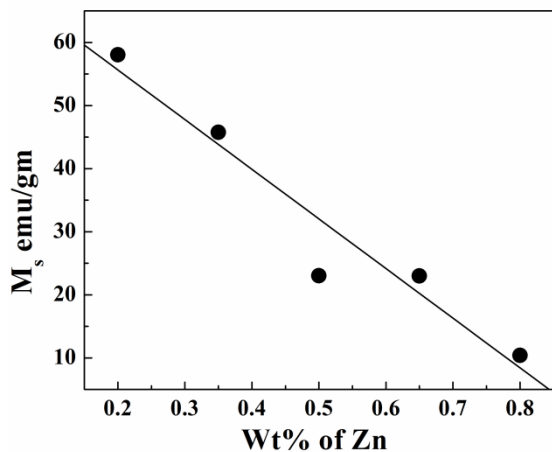


Figure 6: The variation of M_s as function of Zn content change.

The value of squareness ratio (M_r/M_s) is decreases as the Zn content increases as shown in Fig.3.10. This indicates that the system consists of randomly oriented equiaxial particles with cubic magneto crystalline anisotropy [12]. It is well known that the fine particles are easier to be thermally activated to overcome the magnetic anisotropy [13]. When size of the nanoparticles is smaller than the critical size, the blocking temperature, the hysteresis behavior vanishes and the

magnetization direction of the particles simply follows the direction of the applied magnetic field. The hysteresis loops demonstrate a typical superparamagnetic behavior with very low coercivity and remanence. The superparamagnetism of the sample should be attributed to the size of equiaxial shaped nano particles below the super paramagnetic critical size which is near 9 nm. The particle sizes of samples synthesized are mostly smaller than the single domain size so these particles are single domain nanocrystallites. The existence of an effectively uniaxial anisotropy in magnetic nanoparticles has been attributed to surface effects [14] as evidenced by simulations of nanoparticles. Surface effects also tend to lead large anisotropies. The interaction between the core and surface spins leads to a variety of effects including large anisotropy and exchange bias effects.

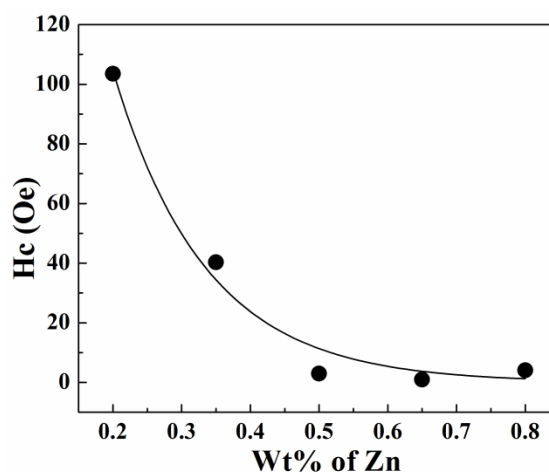


Figure 7: Variation of Coercivity of Zn content change

The values of coercive fields are found to decrease linearly with Zn content increases as shown in Fig 7. But it is interesting to note that the coercivity (103.50 Oe) obtained is lower when compared to the coercivity of Cobalt ferrites (193Oe) reported earlier by Kim et al[15]. The reduction in the magnetic property may be due to the partial substitution of non-magnetic Zn, due to size effect or due to the presence of superparamagnetic particles. The coercivity is found to be maximum when the partial substitution of zinc with cobalt ferrite is minimum.

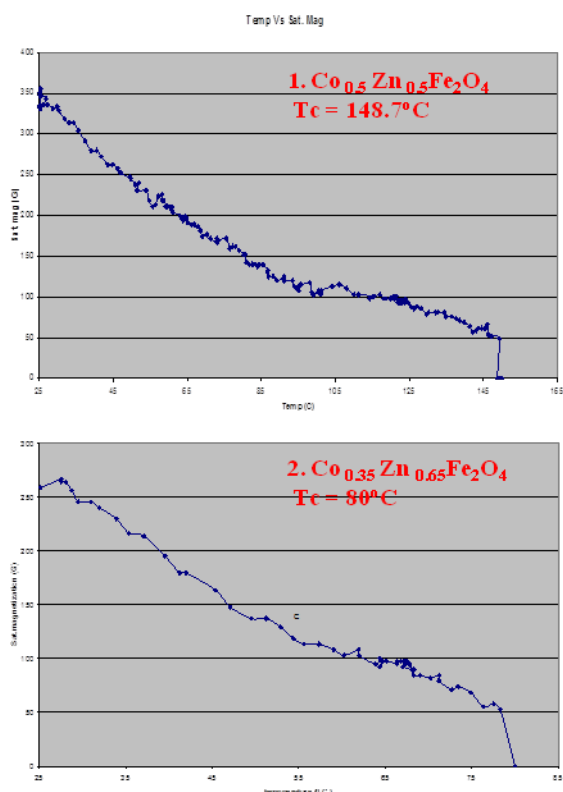


Figure 8: The variation of specific magnetization as function of temperature for the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles.

This coercivity decrease at large particle sizes could be attributed to either of two reasons. First, it may be due to the expected crossover from single domain to multi-domain behavior with increasing size. Second such an effect can arise from a combination of surface anisotropy and thermal energies. We understand the decrease of coercivity with increasing Zn content as being due to the enhanced role of the surface and its strong anisotropy as opposed to the bulk anisotropy. This rise is followed by a decline at small enough sizes when the product of anisotropy energy and volume becomes comparable to the thermal energy, leading to thermally assisted jumps over the anisotropy barriers. It is also likely that the two processes are operating simultaneously and the single domain effects may not be excluded, however the dominant role will be of the surface effects for smaller particles.

2.3 Curie Temperature Measurement On $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ Nanoparticles

The Curie temperature measurements have been carried out using a pulse field magnetometer (PFM) a house made instrument at Ferrite Laboratory, RRCAT, India. From the PFM instrument, we measured specific magnetization as function of temperature as shown in Fig. 8. The measurements were performed in the range of temperature from 5°C to 400°C. The specific magnetization decreases with the increase of the partial substitution of zinc with cobalt. This is typical behavior for superparamagnetic materials as a result of the decrease in the thermal energy.

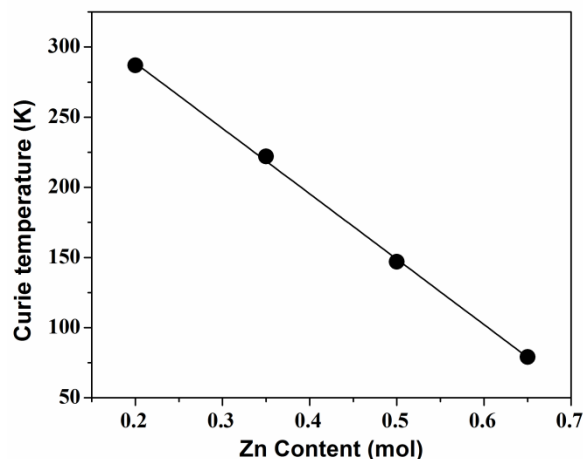


Figure 9: Variation of the Curie temperature with Zn content

The graph of the Curie temperature versus Zn content is shown in Fig.3.13. for different compositions. From the graphs, it is observed that the Curie temperature decreases with the increase of the Zn content. This decrease of the Curie temperature, which is due to the increase of the nonmagnetic Zn substitution with the cobalt, can bring down the Curie temperature close to the room temperature [16].

3. Conclusions

We can say that, The structure of the as prepared samples $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ is found to be spinel structure and which is confirmed using X-ray diffraction analysis. The particle size and its distribution may be controlled by changing the Zn content in the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ investigated by the XRD and HRSEM. The saturation magnetization, which decreased from 58.03 to 10 emu/gm for the increase of Zn content from 0.2 to 0.8 mols at room temperature, appears to be due to pronounced growth of magnetic anisotropy. In magnetization studies, the values of coercivity decreased from 103.5Oe to 0.931Oe as Zn content increased from 0.02 to 0.8. It is observed that the magnetization remanence ratio has decreased from 0.0826 to 0.00048 at room temperature as the Zn content increased to 0.8, suggests that the nanoparticles exhibit an effective anisotropy that is the effective uniaxial anisotropy in magnetic nanoparticles has been explained as arising from surface effects that also lead to large anisotropy energy in nanoparticles. We find that for smaller particles the M_s has a value that was significantly lower than the bulk value, while the larger size particles have values approaching those of bulk. The smaller value of M_s in smaller particles is attributed to the greater fraction of surface spins in the smaller particles.

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