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STRUCTURAL REFINEMENT BY RIETVELD METHOD AND MAGNETIC STUDY OF NANO-CRYSTALLINE CU-ZN FERRITES

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ABSTRACT

A series of nanocrystalline spinel ferrites with chemical compositions $Cu_{1-x}Zn_xFe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) synthesized by wet-chemical co-precipitation method, to investigate their structural and magnetic properties. The structural parameters were measured by applying the full pattern fitting of Rietveld method using Full Prof Program. The crystallite size was calculated by using Scherer formula and Williamson Hall analysis method, and also confirm from by transmission electron microscopy (TEM). The lattice parameter is found to increases with increasing zinc ion concentration. X-ray intensity ratios were calculated in order to determine the possible cation distributions among the tetrahedral (A) and octahedral [B] site. The saturation magnetization (Ms) and Bohr magneton per formula unit (n_B) was measured at room temperature using vibrating sample magnetometer. The Y-K angle increases gradually with increase in Zn^{2+} concentration 'x'. Magnetic AC susceptibility measurements were carried out as a function of temperature in order to measure the Curie temperature (T_C).

PCAS: 75.50.Gg, 75.75.+a, 61.46.Df, 75.40.Cx

KEYWORDS: *Ferrites, Nano-particle, X-ray diffraction, AC susceptibility.*

I. INTRODUCTION

Nano-crystalline ferrites are widely used in many electronic devices such as antenna cores, high frequency inductors, transformer cores, read write heads for high-speed digital taps or disc recordings etc. These are preferred because of their high electrical resistivity, low eddy current losses, high Curie temperature, mechanical hardness, chemical stability and reasonable cost [1-3]. The structural and magnetic properties of ferrites mainly depend upon chemical composition, methods of preparation, sintering temperature and sintering time [4]. A small amount of dopant ion can change structural and magnetic properties of ferrites [5-8]. Among the ferrites, copper ferrites ($CuFe_2O_4$) are extensively investigated because of their interesting cryptographic and magnetic properties [9]. Copper ferrite crystallizes either in a tetragonal (T) or cubic (C) symmetry depending on the cation distribution among sites in its spinel structure [10-11]. The Fe^{3+} ions occupy both tetrahedral (A) and octahedral [B] site. The copper ions occupy only [B] site and causes the tetragonal structure distortions as per Jahn-Teller effect [10-11]. The Cu-Zn ferrites have been studied in the literature due its technological importance [12-15]. The present work deals to investigates the structural and magnetic properties of $Cu_{1-x}Zn_xFe_2O_4$ (x = 0.0 to x =1.0) system via wet-chemical method.

II. EXPERIMENTAL

Nano-ferrites $Cu_{1-x}Zn_xFe_2O_4$ (x = 0.0 to 1.0 in steps of x = 0.2) were synthesized by wet-chemical co-precipitation method. In order to obtain desired composition, stoichiometric amount of corresponding AR grade metal sulphates, were dissolved in distilled water and 2M sodium hydroxide solution was added till pH become 11.5 with constant stirring at a temperature of 60 ºC in oxygen atmosphere. The precipitate was digested for 3 h. at same temperature then filtered and thoroughly washed with distilled water until it becomes free from sodium ions and dried in oven under vacuum. The dried powder mixed homogeneously and annealed at 700 ºC for 6 h. The annealed samples were X-ray examined on Jeol- JDX-8030 at room temperature by using Cu- Kα radiation and TEM analysis was carried out on Philips CM-12 transmission electron microscopy. The refinement of the structure was confirmed by using software WinPLOTR (version LIB-LCSIM). The magnetization and Curie temperature were measured by using vibrating sample magnetometer and AC susceptibility instrument respectively.

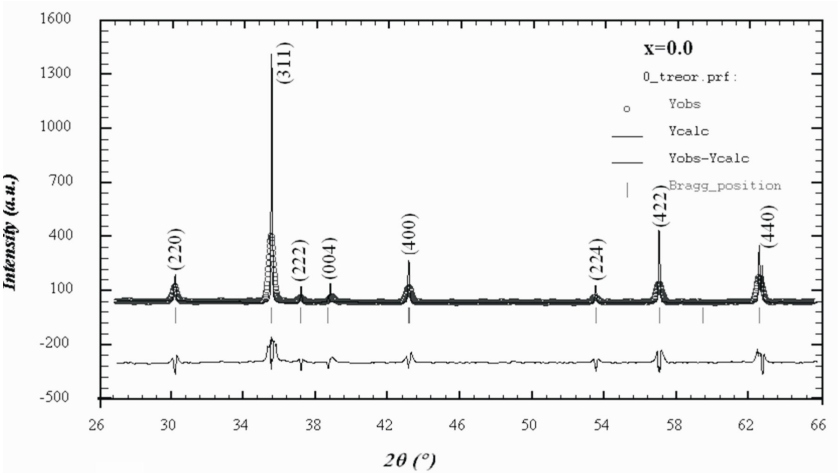
III. RESULT AND DISCUSSION

The X-ray diffraction (XRD) patterns refinement was continuously done until to get goodness factor very close to one. The values of discrepancy factor (R_{wp}) and expected values (R_{exp}) with goodness index are listed in Table 1.

Table 1. The value of discrepancy factor (R_{wp}) goodness factor (χ^2), expected values (R_{exp}), lattice constant (a), phase, particle size (t) of $Cu_{1-x}Zn_xFe_2O_4$ system

Comp. 'x'	R_{wp}	R_{exp}	χ^2	a (Å)			Phase	t (nm)	
				Bragg's	Treor			Scherer's formula	Williamson Hall Analysis
					a	c			
0.0	5.15	2.80	1.84	8.400	8.404	9.504	T	25.6	31.4
0.2	6.87	3.42	2.01	8.412	8.411	8.411	C	27.0	24.6
0.4	6.20	3.52	1.76	8.417	8.417	8.416	C	28.0	28.3
0.6	7.90	3.82	1.64	8.424	8.426	8.403	C	25.2	24.0
0.8	5.94	3.86	1.54	8.431	8.433	8.406	C	27.7	28.1
1.0	3.76	2.54	1.48	8.445	8.445	8.445	C	28.2	28.5

The Rietveld refined XRD pattern for the typical samples (x = 0.0 and 0.2) of $Cu_{1-x}Zn_xFe_2O_4$ systems are shown in Fig. 1. Rietveld refined patterns illustrates the observed and calculated X-ray pattern as well as for their difference for sample x = 0.0 and x = 0.2.



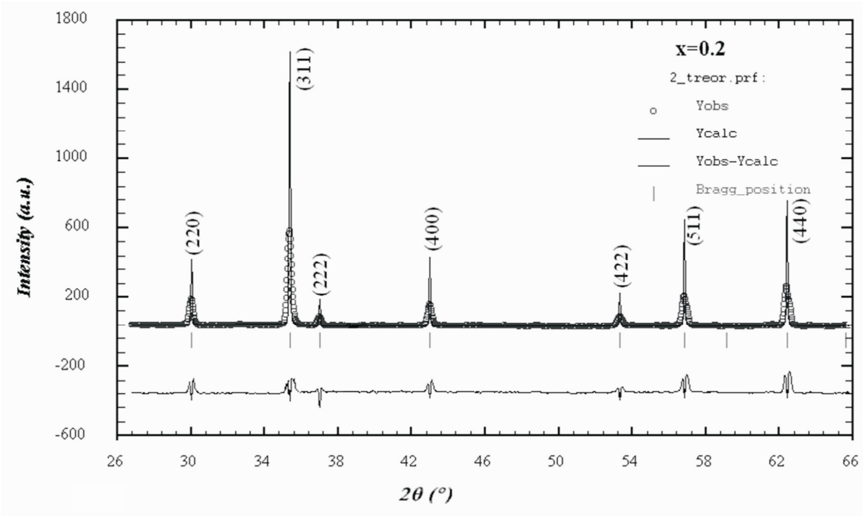


Fig. 1.Observed (°) and calculated (-) X–ray diffraction pattern for sample (x = 0.0 and 0.2)

Analysis of XRD diffraction pattern of all samples confirm the formation of tetragonal structure for x = 0.0, for samples x = 0.2-1.0 it revels the single-phase cubic structure. The tetragonality decreases slowly with increase in Zn content 'x' [16]. The values of lattice constant (a) calculated by using Bragg's law and by Powder X program for Zn substituted copper ferrite are listed in Table 1. Both the values of lattice parameter are good in agreement to each other. Table 1 illustrates that there is an increase in lattice constant with Zn^{2+} ion concentration x, the addition of Zn^{2+} ion in copper ferrite, causes the Fe^{3+} ions migrate from (A) site to [B] site, the Zn^{2+} ion being larger ionic radius (0.81 Å) than that of Fe^{3+} ion (0.67 Å). Zn^{2+} ions replaces Fe^{3+} from (A) site and its results there is expansion in lattice constant [12]. The tetragonal distortion of copper ferrite from cubic spinal structure, due to absence of Fe^{3+} ions at tetrahedral sites, this distortion explain by Jahn- Teller theory according to it, a non liner molecule in ground state is unstable in the symmetric configuration, it will distort it self to lower its energy. The ions with d^4 or d^9 electronic configuration, when situated at octahedral site causes a strong tetragonal distortion (c/a.>1). Similarly the ions with d^3 and d^8 configuration and located at tetrahedral site produce a tetragonal distraction with (c/a.>1), at tetrahedral site the ions with d^3 and d^8 configuration also produce tetragonal distortion with c/a>1 [13].

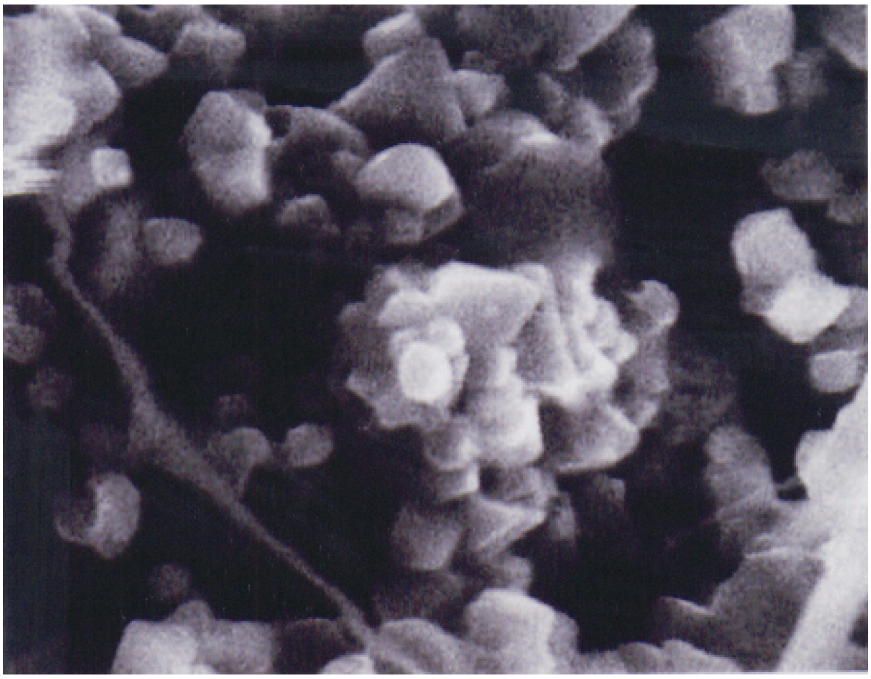


Fig. 2. Scanning electron micrograph for sample (x = 0.6)

Figure 2 shows scanning electron micrographs (SEM) of the typical sample (x = 0.6). The SEM image indicating the fracture surface, further the texture was homogenous structure constiting polyhedral grain with well defined grain boundaries. The average crystallite size for each sample was determined using Scherrer formula [17] and also calculated by Williamson's Hall analysis [18]. Crystallite size obtained by both the method shows good agreement with each other (Table 1). The morphology of synthesized sample is studied by TEM as shown in Fig. 3 (x = 0.4). It observed that the particle obtained in the range of 25 to 32 nm.

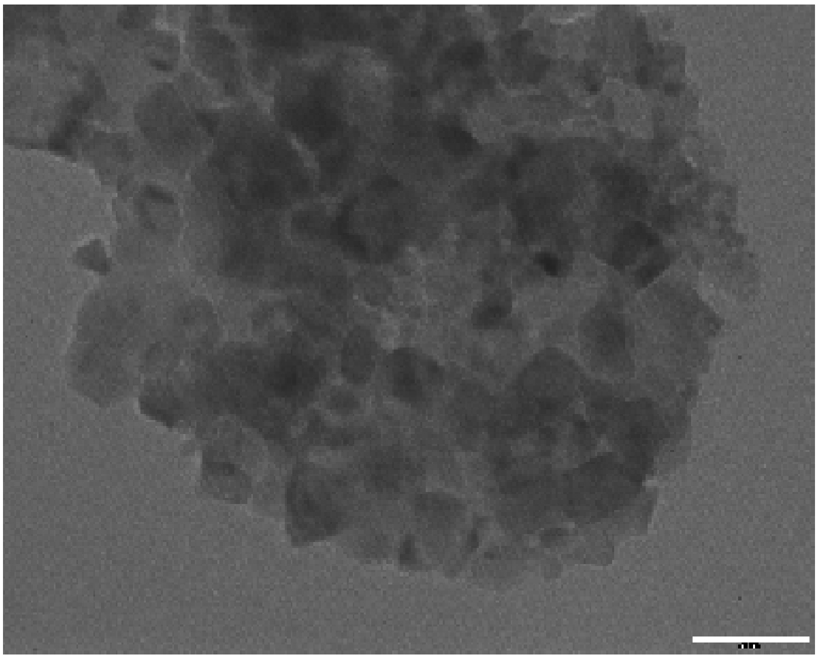


Fig. 3. Transmission electron micrograph for sample (x = 0.4)

The cation distributions for the system $Cu_{1-x}Zn_xFe_2O_4$ were determined by X-ray diffraction method. In order to determine the cation distribution. The X-ray intensity was calculated using the formula suggested by M.G. Burger [19]. The X-ray intensity ratios I(220)/I(400) and I(422)/I(440) were calculated for various possible compositions of cations and compare with observed intensity ratios. The combinations of cation for which observed and calculated intensity ratio agree close to each other are taken to be corrected cation distributions which are listed in Table 2.

Table 2. Cation distribution and X- ray intensity ratio for oCu_{1-x} Zn $_x$$Fe_2O_4$ system.

`x`	Cation distribution		Intensity ratio			
			I_{220}/I_{400}		I_{422}/I_{440}	
	A- site	B- site	Obs.	Cal.	Obs.	Cal.
0.0	$(Cu_{0.0}Fe_{1.0})$	$[Cu_{1.0}Fe_{1.0}]$	1.1428	1.1646	0.3809	0.1960
0.2	$(Cu_{0.0}Zn_{0.2}Fe_{0.8})$	$[Cu_{0.8}Zn_{0.0}Fe_{1.2}]$	1.1785	1.4700	0.3260	0.2099
0.4	$(Cu_{0.0}Zn_{0.4}Fe_{0.6})$	$[Cu_{0.6}Zn_{0.0}Fe_{1.4}]$	1.3461	1.4981	0.3061	0.2128
0.6	$(Cu_{0.0}Zn_{0.6}Fe_{0.4})$	$[Cu_{0.4}Zn_{0.0}Fe_{1.6}]$	1.6500	1.7143	0.3809	0.2395
0.8	$(Cu_{0.0}Zn_{0.8}Fe_{0.2})$	$[Cu_{0.2}Zn_{0.0}Fe_{1.8}]$	1.3636	1.9485	0.3500	0.2560
1.0	$(Cu_{0.0}Zn_{0.5}Fe_{0.5})$	$[Cu_{0.0}Zn_{0.5}Fe_{1.5}]$	1.5714	1.5854	0.2916	0.2356

Table 2 indicates that the Zn ions occupy (A) site for the samples x = 0.2-0.8. The Zn cation prefers to situate at (A) site as the Cu concentration decreases from [B] site, at the same time Fe cation shifts from tetrahedral (A) site to octahedral [B] site in order to balance the relative occupancy by the space group [20]. For x = 0.2 to x = 0.8, zinc shows a preference for tetrahedral (A) site where their 4S, 4P or 5S, 5P electron respectively can perform covalent bond with the 2 P electron of oxygen ions.

The magnetic properties of $Cu_{1-x}Zn_xFe_2O_4$ system were studied by hysteresis loop techniques and AC susceptibility measurements. The saturation magnetization (M_s) and magneton number (n_B) were measured at room temperature with the help of hysteresis loops. The observed magneton number (n_B Obs.) were calculated using the relation,

$$n_B = \frac{M_w \times M_s}{5585} \qquad (1)$$

where M_w is molecular weight of the composition and M_s is saturation magnetization.
According to the Neel's two sublattices model of ferrimagnetisms, the calculated magnetic moment (n_B Cal.) per unit formula in μ_B, n_B^N is expressed as,

$$n_B^N = M_B(x) - M_A(x) \qquad (2)$$

where, MA and MB are the A and B sublattice magnetic moment in B.

Table 3. Compositional variation of Saturation magnetization (Ms), Magneton number (n_B) and Y-K angle (Y-K) of $Cu_{1-x}Zn_xFe_2O_4$ system

Comp. 'x'	Ms (emu/gm)	n_B (μ_B) Obs.	cal	Y-K (degree)
0.0	38.85	1.66	1.0	--
0.2	62.16	2.66	2.8	---
0.4	108.78	4.67	4.6	---
0.6	62.16	2.67	6.4	56.22
0.8	38.85	1.67	8.2	73.13
1.0	23.31	1.00	5.0	62.18

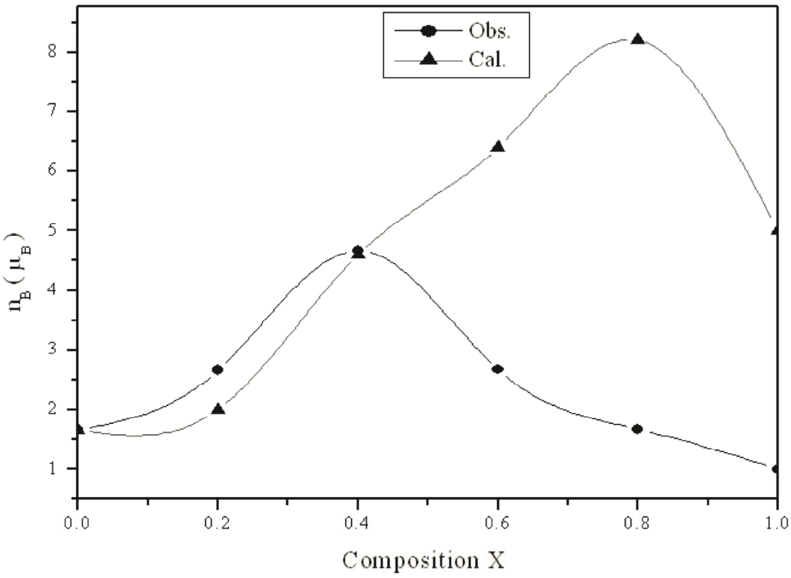


Fig.4. Variation of magneton number (n_B), observed and calculated with Zn content (x).

The values of Neel's magnetic moment n_B^N were calculated by taking ionic magnetic moment of Fe, Cu and Zn. The values of saturation magnetization 'Ms' and magneton number 'n_B' are represented in Table 3. It is observed from Table 3 and Fig. 4 that both the values 'Ms' and 'n_B' increases up to x = 0.4 then decrease as ' x ' increases. Since the diamagnetic Zn^{2+} ions replaces Fe^{3+} ions at tetrahedral (A) site due to the prominent inter-sub lattice A-B interaction up to x = 0.4 the net magnetic moment is increased.

The behavior of magnetic moment n_B is also explained on the basis of Neel's theory [21] and the calculated 'n_B' value of spin moment and also by Neel's two sub-lattice model. The observed and calculated magnetic moment values 'n_B' are similar to each other for x = 0.4, estimating that the structure is collinear, then x = 0.4 the observed 'nB' values are lower then calculated values. The reason for this decrease in magnetic moment after x = 0.4 can explain on basis of Yafet-Kittle angle [22]. These low magnetic moments can be explained in term of non-collinear spin arrangement that is the presence of a small canting of [B] site moment with respect to distortion of (A) site. [23]. The values of Yafet-Kittle angle were calculated using relation discussed elsewhere [24], and their values are presented in Table 3.

The temperature dependence AC susceptibility measurements for all the samples are shown in Fig. 5. Theoretical calculation of Curie temperature for Zn substituted copper ferrites was obtained by Upadhya's model [25]. The Curie temperature is depends upon the number of active magnetic linkages per magnetic ion per formula unit. Curie temperature calculated by using relation [26].

$$T_C = \frac{M_{(x=0)} \times T_{c(X=0)} \times n_x}{n_{(x=0)} \times M_x} \qquad (3)$$

where M(x) is the relative weighted total magnetic ions per unit formula, calculated by considering the weighing of magnetic ion M' to that of ions as µM'/µFe' where µM' and µFe' are magnetic moments of M' and iron ions respectively.

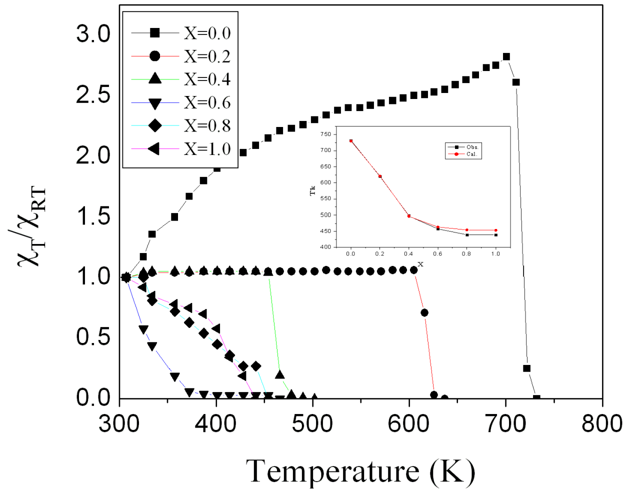


Fig. 5. Variation of χ_T/χ_{RT} versus temperature. The inset is the variation of Curie temperature versus Zn content (x).

The observed Curie temperature and Curie temperature calculated theoretically both are given in the inset of Fig. 5. It is observed that χ_T / χ_{RT} fall sharply, when magnetic state of sample changes from ferri-magnetic to para-magnetic. The magnetic properties of Cu1-xZnxFe2O4 system strongly depends upon Zn^{2+} ion concentration. The change in Curie temperature is due to influences of cation stoichiometry and their specific sites. The decrease in Curie temperature with the increase in Zn^{2+} may be explained by A-B exchange interactions. The decrease in Curie temperature due to weak A-B interactions, low magnetic linkages, and can be attributed to increase in distance of magnetic moment of (A) and [B] sites. The observed and calculated Curie temperature values agree with each other.

IV. CONCLUSIONS

Homogeneous nano-ferrite Cu1-xZnxFe2O4 system was synthesized by simple and economical wet chemical method. In the present study Zn^{2+} ions causes change in structural and magnetic properties of copper ferrite, initially $CuFe_2O4$ is tetragonal then its phase changes to cubic as Zn content x increases. The unit cell parameter also increases with Zn content x. The particle sizes calculated by different methods are fairly agrees with each other. The Y-K angle increases with Zn content x. The calculated and observed values of magneton number are not agreed close to each other for x > 0.4, suggesting that the structure is non-collinear. The decrease in Curie temperature with Zn content x is due to the decreases in magnetic linkages.

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