

## Structural and magnetic properties of zinc- and aluminum-substituted cobalt ferrite prepared by co-precipitation method

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**Abstract.** Spinel ferrites having the general formula  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_{2-x}\text{Al}_x\text{O}_4$  ( $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$ ) were prepared using the wet chemical co-precipitation technique. The samples were annealed at  $800^\circ\text{C}$  for 12 h and were studied by means of X-ray diffraction, magnetization and low field AC susceptibility measurements. The X-ray analysis showed that all the samples had single-phase cubic spinel structure. The variation of lattice constant with Zn and Al concentration deviates from Vegard's law. The saturation magnetization  $\sigma_s$  and magneton number  $n_B$  measured at 300 K using high field hysteresis loop technique decreases with increasing  $x$ , suggesting decrease in ferrimagnetic behaviour. Curie temperature  $T_C$  deduced from AC susceptibility data decreases with  $x$ , suggesting a decrease in ferrimagnetic behaviour.

**Keywords.** Ferrite; co-precipitation; magnetization; AC susceptibility.

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### 1. Introduction

The method of preparation plays a very important role with regard to the chemical, structural and magnetic properties of spinel ferrite [1]. Ferrites are commonly produced by a ceramic process involving high temperature solid state reaction between the constituent's oxides/carbonates. The particles obtained by ceramic method are rather large and of varying size which result in non-reproducible ferrites in terms of their properties. In order to overcome these difficulties, wet chemical methods like air oxidation [2], co-precipitation [3,4], hydrothermal processing etc. [5,6] have been considered which give homogeneous, fine and reproducible ferrites.

The cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) possesses an inverse spinel structure and the observed degree of inversion depends upon heat treatment [7]. It is well-known that when ferrites are sufficiently diluted with non-magnetic atoms, they can show

a wide spectrum of magnetic structures, ferrimagnetic order, cluster spin glass etc. [8].

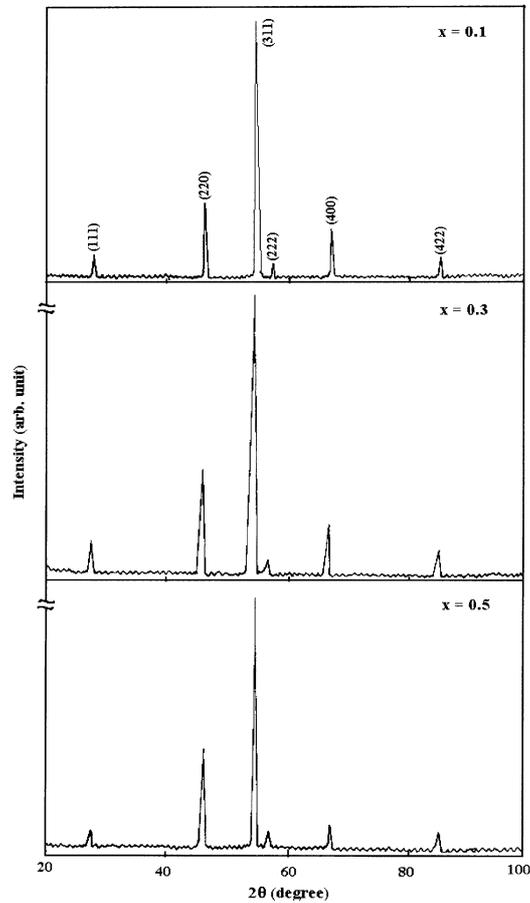
No systematic investigations of the structural, electrical and magnetic properties of  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_{2-x}\text{Al}_x\text{O}_4$  for  $x = 0.0\text{--}0.6$  prepared by wet chemical co-precipitation have been reported in the literature. Though, structural and magnetic properties of  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  [9] and  $\text{CoFe}_{2-x}\text{Al}_x\text{O}_4$  [10,11] ferrite system prepared by co-precipitation method have been studied separately, no attempt has been made to study the simultaneous dilution of tetrahedral (A) site and octahedral (B) site by adding zinc ( $\text{Zn}^{2+}$ ) in place of cobalt ( $\text{Co}^{2+}$ ) and aluminum ( $\text{Al}^{3+}$ ) in place of ferric ( $\text{Fe}^{3+}$ ) ions respectively in cobalt ferrite.

The aim of the present paper is to synthesize Zn- and Al-substituted cobalt ferrites ( $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_{2-x}\text{O}_4$ ) by wet chemical co-precipitation technique and to investigate the effect of simultaneous substitution of Zn and Al on the structural and magnetic properties of cobalt ferrites.

This paper reports the synthesis of  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_{2-x}\text{O}_4$  ( $x = 0.0\text{--}0.6$ ) and study of structural and magnetic properties of this system (Co–Zn–Fe–Al) through X-ray diffraction, magnetization and AC susceptibility measurements. Further, the properties of  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_{2-x}\text{Al}_x\text{O}_4$  (Co–Zn–Fe–Al) will be compared with those of  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  (Co–Zn) [9] and  $\text{CoFe}_{2-x}\text{Al}_x\text{O}_4$  (Co–Al) [10,11] systems, prepared by wet chemical co-precipitation technique and annealed at  $800^\circ\text{C}$ .

## 2. Experimental

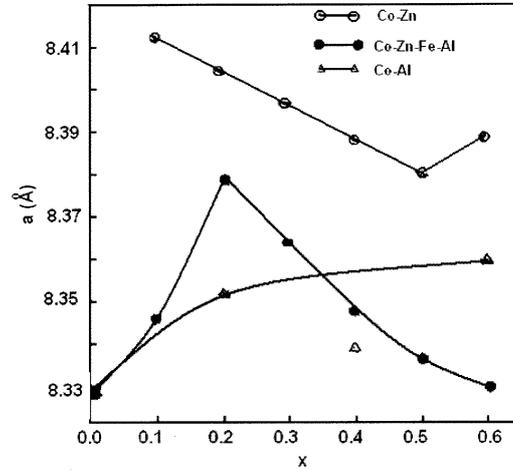
The spinel ferrite system  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_{2-x}\text{Al}_x\text{O}_4$  with variable composition ( $x = 0.0\text{--}0.6$ ) is prepared by air oxidation of an aqueous suspension containing  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  cations in proper proportion. The starting solutions were prepared by mixing 50 ml of aqueous solution of  $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ ,  $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ ,  $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3\cdot 16\text{H}_2\text{O}$  in stoichiometric proportions. A two molar (2 M) solution of NaOH was prepared as a precipitant. It has been suggested that the solubility product constant  $K_{\text{sp}}$  of all the constituents always exceed when the starting solution is added into the precipitant. Therefore, in order to achieve simultaneous precipitation of all the hydroxides,  $\text{Co}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_2$ , the starting solution ( $\text{pH} \approx 3$ ) was added to the solution of NaOH and a suspension ( $\text{pH} = 11$ ) containing dark intermediate precipitation was found. Then the suspension was heated and kept at a temperature of  $60^\circ\text{C}$ , while oxygen gas was bubbled uniformly into the suspension to stir it and to promote the oxidation reaction until all the intermediate precipitant changed into the dark brownish precipitate of the spinel ferrite. The samples were filtered and washed several times by distilled water. The wet samples of Co–Zn–Fe–Al system were annealed at  $800^\circ\text{C}$  for 12 h. The X-ray powder diffraction patterns were recorded using  $\text{Cu-K}_\alpha$  radiation on Philips X-ray diffractometer (PW 3710). The saturation magnetization of each sample was measured using a high field hysteresis loop technique [12]. The low field AC susceptibility measurements on powder samples were carried out in the temperature range 300–800 K using double coil set-up [13] operating at a frequency of 263 Hz in the rms field of  $39.8 \text{ A}\cdot\text{m}^{-1}$ .



**Figure 1.** Typical X-ray diffraction pattern for Co-Zn-Fe-Al ( $x = 0.1, 0.3, 0.5$ ).

### 3. Results and discussion

The X-ray diffraction pattern of all the samples showed the formation of single-phase spinel structure. A representative XRD pattern indicating  $(hkl)$  values of each peak is shown in figure 1. The values of lattice constant  $a$  determined from X-ray data analysis with an accuracy of  $\pm 0.002 \text{ \AA}$  for  $x = 0.0-0.6$  are given in table 1. The plot of lattice constant  $a$  ( $\text{\AA}$ ) vs. zinc and aluminum content  $x$  is depicted in figure 2. It is found from figure 2 that lattice constant initially increases up to  $x = 0.2$  and thereafter it decreases with further increase in  $x$ . This indicates that the variation of  $a$  with  $x$  does not obey Vegard's law [14]. This nonlinear behaviour of  $a$  with  $x$  may be due to substitutional effect of larger  $\text{Zn}^{2+}$  ions ( $0.82 \text{ \AA}$ ) and smaller  $\text{Al}^{3+}$  ion ( $0.51 \text{ \AA}$ ) in cobalt ferrite. Further, nonlinear behaviour of  $a$  with  $x$  on the other hand, is reported for the systems which are not completely normal or inverse [15]. The variation of  $a$  with  $x$  of Co-Zn-Fe-Al system is compared with



**Figure 2.** Variation of lattice constant  $a$  with composition  $x$ .

Co-Zn and Co-Al systems and the same is represented in figure 2. It is observed from figure 2 that for Co-Zn, lattice constant decreases up to  $x = 0.5$  then it increases and for Co-Al ferrite system, lattice constant increases with  $x$ , whereas for Co-Zn-Fe-Al ferrite system it increases initially and then decreases with  $x$ .

The X-ray density  $d_x$  for all the samples has been calculated from the molecular weight and the value of unit cell. The values of X-ray density are given in table 1. The XRD line width and particle size are connected through the Scherrer equation [16].

$$t = 0.9\lambda/B \cos \theta_B \quad \text{with } B^2 = B_a^2 - B_b^2, \quad (1)$$

where  $t$  is the particle diameter,  $\lambda$  is the wavelength of the X-ray radiation,  $B$  is the measure of the broadening of diffraction due to size effect,  $B_a$  and  $B_b$  are the full-width at half-maximum of the XRD line of the sample of a standard specimen respectively at around the same Bragg's angle and  $\theta_B$  is the Bragg's angle. Using this relation (eq. (1)), the particle sizes, for all the samples have been estimated and are given in table 1.

The saturation magnetization ( $\sigma_s$ ) and the magneton number  $n_B$  (the saturation magnetization per formula unit in Bohr magneton) at 300 K obtained from magnetization data for  $x = 0.0-0.6$  are summarized in table 2. From the field dependence of the magnetization and observed magnetic moments (table 2) it is clear that the samples with  $x = 0.1-0.6$  show ferrimagnetic behaviour, which decreases with increase in  $x$  value. Figure 3 shows the variation of  $n_B$  with  $x = 0.0-0.6$  at 300 K. It is observed that  $n_B$  increases up to  $x = 0.3$  and then decreases. In the present system Co-Zn-Fe-Al,  $Zn^{2+}$  ions replaces  $Fe^{3+}$  ions at A-site whereas  $Fe^{3+}$  ions are replaced by  $Co^{2+}$  and  $Al^{3+}$  ions. As a result magnetic moments of B sub-lattice and A sub-lattice decrease. But differences of magnetic moment of A and B sub-lattices increase and as a result  $n_B$  increases. For  $x > 0.3$ , it is observed that  $n_B$  decreases which may be due to the presence of spin canting. Consequently, the value of  $n_B$

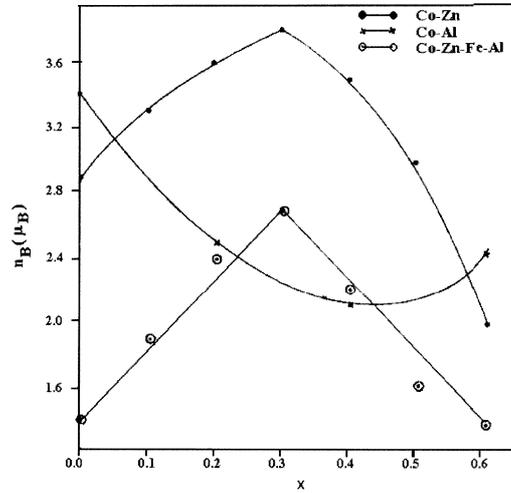


Figure 3. Variation of magneton number  $n_B$  with the composition  $x$ .

which is the difference between  $m_B$  and  $M_A$  increases for smaller concentration, i.e. up to  $x = 0.3$  but for higher concentration of  $x$  ( $x > 0.3$ )  $n_B$  decreases with  $x$  which is due to the weakening of A–B interaction and consequently stronger B–B interaction.

According to the literature, cobalt ferrite is an inverse ferrite [16] assuming that  $Zn^{2+}$  ions have strong preference for tetrahedral A-site and  $Al^{3+}$  can occupy octahedral B-sites. The cation distribution for  $Co_{1-x}Zn_xFe_{2-x}Al_xO_4$  ferrite system can be written as



According to the Neel's [17] two sub-lattice model of ferrimagnetism, Neel's magnetic moment per formula unit in  $\mu_B$  is expressed as

$$n_B = M_B(x) - M_A(x), \quad (3)$$

where  $M_B$  and  $M_A$  are the B and A sub-lattice magnetic moments in  $\mu_B$ . The  $n_B^N$  values of the system  $Co_{1-x}Zn_xFe_{2-x}Al_xO_4$  were calculated using the cation distribution (eq. (2)) and ionic magnetic moments of  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$  and  $Al^{3+}$  with their respective values  $5 \mu_B$ ,  $3 \mu_B$ ,  $0\mu_B$  and  $0\mu_B$ . The calculated values of  $n_B^N$  using the cation distribution (eq. (2)) and Neel's eq. (3), for  $x = 0.0-0.6$  are given in table 2. It is found from table 2 that the calculated values of  $n_B$  are not in good agreement with the observed values of  $n_B$ , suggesting that significant canting exists at octahedral B sites which can be explained on the basis of three sub-lattice model suggested by Yafet–Kittel [18]. Yafet–Kittel (Y–K) angles can be obtained from the variation of  $n_B$  with  $x$  using the relation,

$$n_B = M_B \cos \alpha_{YK} - M_A. \quad (4)$$

The values of Y–K angles thus obtained are given in table 2.

**Table 1.** Lattice constant, X-ray density and particle size for  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_{2-x}\text{Al}_x\text{O}_4$ .

Composition $x$	Lattice constant $a$ (Å)	X-ray density $d_x$ (g/cm <sup>3</sup> )	Particle size (nm)
0.0	8.332	5.396	31
0.1	8.346	5.308	40
0.2	8.379	5.195	28
0.3	8.364	5.172	60
0.4	8.348	5.151	22
0.5	8.337	5.120	25
0.6	8.330	5.081	25

Figure 4 shows that the temperature dependence of the AC susceptibility  $\chi_{AC}(T)$  for typical samples ( $x = 0.1, 0.3$  and  $0.5$ ). The result shows that there exists a magnetic ordering. A close analysis of  $\chi_T/\chi_{RT}$  plots exhibits two peaks, one sharp near the Curie temperature ( $T_C$ ) and another broad peak at much lower temperature for  $x = 0.1$ . This behaviour of AC susceptibility can be explained on the basis of magnetic ordering in the system. Many workers [19–21] have reported that temperature dependence of AC susceptibility for cobalt ferrite shows two peaks. The second peak (at  $\approx 400$  K) observed in pure cobalt ferrite is referred to as the isotropic peak, which could be seen clearly for a magnetic material in a multi-domain state, if the material has a temperature at which magneto-crystalline isotropy is zero [22]. According to Bean [23], the susceptibility is inversely proportional to the coercive force. Therefore, the increase in susceptibility after the isotropic peak is attributed to a decrease in coercive force. The existence of a coercive force clearly indicates that the samples contain clusters of different sizes and each spin cluster should be large since a very large blocking temperature is observed. Further, as  $x$  increases isotropic peak diminishes. Simultaneous substitution of Zn and Al in cobalt ferrite reduces the coercive force and as a result peak value decreases. The Curie temperature  $T_C$  determined from the plots  $\chi_T/\chi_{RT}$  are given in table 2. Figure 5 depicts the variation of the Curie temperature ( $T_C$ ) with Zn and Al concentration ( $x$ ) obtained from AC susceptibility data. It is observed from table 2 that there is a decrease in Curie temperature with the addition of Zn and Al content  $x$  indicating the reduction in ferrimagnetic behaviour. This is attributed to decrease in A–B interaction resulting from the replacement of  $\text{Fe}^{3+}$  ions by  $\text{Al}^{3+}$  ions at octahedral B sites and  $\text{Co}^{2+}$  ions by  $\text{Zn}^{2+}$  ions at tetrahedral A sites.

The behaviour of Curie temperature with simultaneous substitution of Zn and Al in cobalt ferrite is compared with Zn- and Al-substituted cobalt ferrite separately (figure 5). In each case it has been found that Curie temperature decreases with concentration  $x$ . Further, it can be observed from figure 5 that the decrease in  $T_C$  with  $x$  is faster for Co–Zn–Fe–Al system than for Co–Zn and Co–Al systems. This may be due to simultaneous dilution of A and B sub-lattice by non-magnetic Zn and Al respectively.

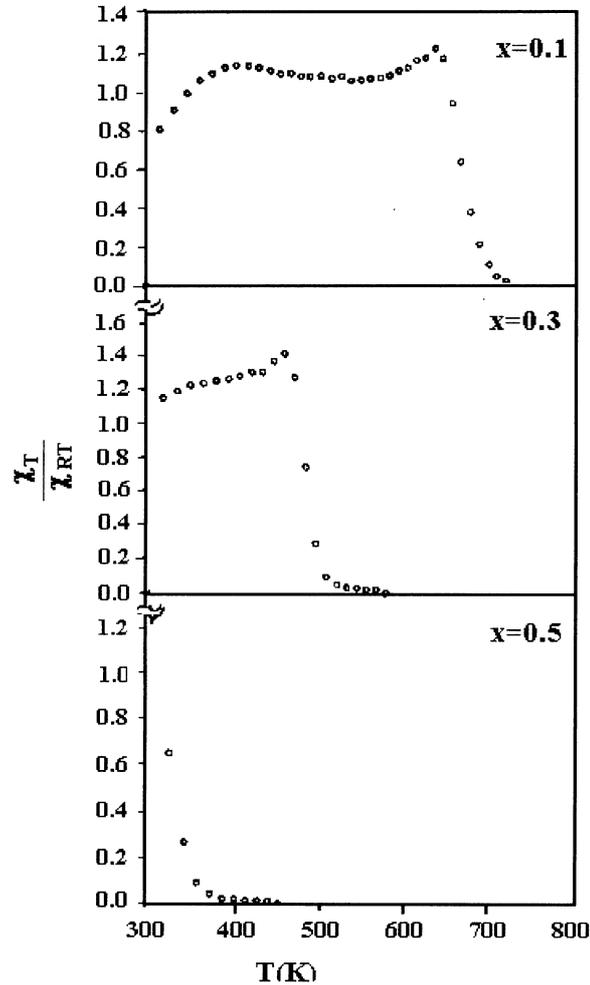
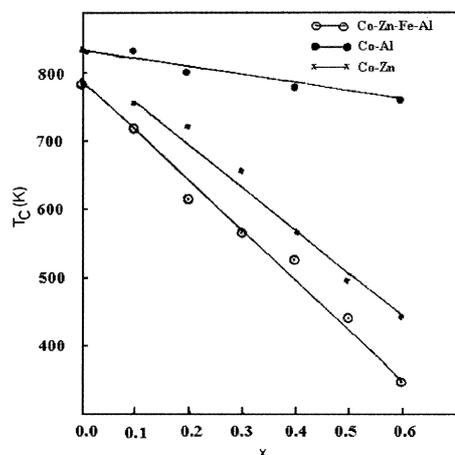


Figure 4. Temperature dependence of the AC susceptibility ( $x = 0.1, 0.3, 0.5$ ).

#### 4. Conclusion

Wet chemical co-precipitation method plays an important role in governing the properties of the ferrite system. The simultaneous substitution of non-magnetic  $Zn^{2+}$  and  $Al^{3+}$  has strong influence on the structural and magnetic properties of cobalt ferrite as compared to Zn and Al separately substituted cobalt ferrite. The lattice constant obtained from XRD data shows non-linear behaviour. The observed and calculated values of magneton number from each other suggesting that significant canting exists at octahedral B sites. The rate of decrease of Curie temperature is fast for Co-Zn-Fe-Al system as compared to Co-Zn and Co-Al systems.



**Figure 5.** The variation of Curie temperature with composition  $x$ .

**Table 2.** Saturation magnetization, magneton number and Curie temperature for  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_{2-x}\text{Al}_x\text{O}_4$ .

Composition $x$	Saturation magnetization $\sigma_s$ (emu/gm)	Magneton number $n_B$ ( $\mu_B$ )		Yafet-Kittel angle $\alpha_{\text{YK}}$ ( $^\circ$ )	Curie temperature $T_C$ (K)
		Obs.	Cal.		
0.0	34.00	1.41	3.00	36.75	790
0.1	46.24	1.92	3.20	33.51	730
0.2	59.80	2.47	3.40	29.04	617
0.3	61.20	2.50	3.60	32.32	578
0.4	54.40	2.20	3.80	40.12	543
0.5	40.80	1.63	4.00	50.55	450
0.6	34.00	1.35	4.20	56.06	349

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