

STRUCTURAL AND PHYSICAL PROPERTIES OF ZN SUBSTITUTED COBALT FERRITES

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ABSTRACT

A series of samples of $Co_{1-x}Zn_xFe_2O_4$ (with $x = 0.0$ to 1.0 in the steps of 0.1) were prepared by the standard double sintering ceramic technique using high purity oxides such as Fe_2O_3 , Co_3O_4 and ZnO . The samples were sintered at $1100^\circ C$ for 2h. From the analysis of XRD patterns the sample indicates the single phase cubic spinel structure. The lattice parameter 'a' is found to increase linearly with the increase of Zn content following the Vegard's law. The bulk density is lower than the X-ray density. This may be due to existence of pores, which were formed and developed during the sample preparation or the sintering process. Density is observed to increase with increasing Zn content whereas the porosity decreases. The compositional dependence of Curie temperature T_c was obtained from the permeability versus temperature of different composition. The Curie temperature was observed to decrease with increasing Zn content. Increase in the non-magnetic Zn ions reduces the magnetic moment of the A sublattice as the Zn ions preferentially occupy the A sites of the spinel lattice thereby reducing the A-B exchange interaction between A and B sublattices. This results in a reduction in Curie temperature.

Keywords: Ferrites, Lattice parameter, Porosity, Bulk density.

1. INTRODUCTION

The spinel ferrite belongs to an important class of magnetic materials because of their remarkable magnetic properties, particularly in radio frequency region, physical flexibility, high electrical resistivity, mechanical hardness and chemical stability (Rajath *et al.*, 2008; Lee *et al.*, 1998; Sharma *et al.*, 2006). Ferrites exhibit a substantial spontaneous magnetization at room temperature, like the normal ferromagnetic. They have two unequal sub-lattices called tetrahedral (A-site) and octahedral (B-site) and are ordered antiparallel to each other. In ferrites the cations occupy the tetrahedral (A) and octahedral (B) sites of the cubic spinel lattice and experience competing nearest neighbour (J_{AB}) and the next nearest neighbour (J_{AA} and J_{BB}) interactions with $|J_{AB}| \gg |J_{BB}| > |J_{AA}|$. The magnetic properties of ferrites are dependent on the type of magnetic ions residing on the A and B sites and the relative strengths of the inter (J_{AB}) and intrasublattice (J_{BB} , J_{AA}) interactions. Ferrites are ferrimagnetic cubic spinels and possess combined properties of magnetic materials and insulators. They have been extensively investigated and are subject of great interest because of their importance in many technological applications from both the fundamental and the applied research points of view. The important structural and magnetic properties of these spinels are responsible for their applications in various fields. The magnetization behavior and magnetic ordering of Zn substituted Co-Zn, Cu-Zn, Ni-Zn and Mg-Zn ferrites have been studied by many workers (Pettit *et al.*, 1971; Kulkarni *et al.*, 1982; Satyamurthy *et al.*, 1969; Manjurul Haque *et al.*, 2009), extensive work has been performed on the solid solution of $Co_{1-x}Zn_xFe_2O_4$, x ranging from 0.0-1.0. But the exact nature of magnetic ordering for all the composition is not very clear. Magnetic properties of Co-Zn ferrites have been reported only for particular value of x or limiting values (Bhowmik *et al.*, 2002; Wang Li *et al.*, 2008). Zn substituted spinel ferrites showed good magnetic properties which are characterized by a maximum in saturation magnetization in certain composition (Girigis, 1993; Gulliot *et al.*, 1988; Wafik *et al.*, 1990). The partial replacement of nonmagnetic Zn ions in cobalt ferrite is expected to weaken the magnetic coupling resulting in decrease of Curie temperature. Some work has been reported on mixed Co-Cd ferrites (Gobal *et al.*, 2004; Ghani *et al.*, 1991). Co-Zn ferrites are quite important in the field of microwave industry where a mixture of $CoFe_2O_4$ with long range ferromagnetic ordering with $T_c \approx 520^\circ C$ and $ZnFe_2O_4$ with antiferromagnetic ordering having Neel temperature $T_N \approx 9K$. Zinc is known to play a decisive role in determining the ferrite properties (Smit *et al.*, 1959).

Hence the compositional variation in the ferrites has been brought about by varying the Zn content. When Co^{2+} is replaced by Zn^{2+} in $Co_{1-x}Zn_xFe_2O_4$, $ZnFe_2O_4$ and $CdFe_2O_4$ are generally assumed to be normal spinel with all Fe^{3+} ions on B-sites and all Zn^{2+} and Cd^{2+} ions on A sites (Brabers *et al.*, 1995; Goldman, 1990). Thus, with increasing x, the Fe_A-O-Fe_B interaction becomes weak and T_c is expected to decrease. The present work focuses on the effect of Zn^{2+} substitution on the structural and physical properties of Co-Zn ferrite.

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A series of polycrystalline samples $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (with $x = 0.0$ to 1.0 in the steps of 0.1) was prepared by the standard double sintering ceramic methods at the Materials Science Division, Atomic Energy Centre, Dhaka. The weight percentage of the oxide to be mixed for various samples was calculated by using formula:

$$\text{Weight \% of oxide} = \frac{M.\text{wt. of oxide} \times \text{required weight of the sample}}{\text{Sum of Mol. wt. of each oxide in a sample}}$$

Intimate mixing of the materials was carried out using agate mortar for 4 hrs and then ball milled in a planetary ball mill in ethyl alcohol media for 2 hrs with stainless steel balls of different sizes in diameter. The slurry was dried and the powder was pressed into disc shape. The disc shaped sample was pre-sintered at 950°C for 5 hrs. After that samples were crushed again and subsequently wet ball milled for 6 hrs. The powder was again dried and pressed into pellet and toroid shape respectively under pressure of 1.76 and 1.2 ton-cm^{-2} . The prepared samples were sintered at 1100°C for 2 hrs with a microprocessor controlled muffle furnace. Single-phase cubic spinel structure was confirmed by X-ray diffraction using Phillips (PW 3040) X'pert PRO X-ray diffractometer. Temperature dependence of initial permeability of the toroid samples was measured with the Hewlett Packart impedance analyzer (HP4192A).

3. RESULTS AND DISCUSSIONS

A phase analysis using x-ray diffraction (XRD) technique was performed to confirm the formation of single-phase cubic spinel structure as shown in Fig.1. The XRD pattern of all the samples of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ with the (hkl) values corresponding to the diffraction peaks of different planes (111), (220), (311), (222), (400), (422), (511), and (440) which represent either odd or even indicating the samples are spinel phase. The peaks are found to shift slightly towards the lower d-spacing values. Therefore single phase spinel structure is confirmed for all the samples with increasing trend of the lattice parameter as the Zn content is increased. Since no ambiguous reflections other than the spinel structures are evidenced, this demonstrates the homogeneity of the prepared samples.

The lattice parameter of all the samples has been precisely determined considering the reflections with the CuK_α components using the extrapolated Nelson-Riley function $F(\theta) = 0$ at $\theta = 90^\circ$ (Nelson *et al.*, 1945),

$$F(\theta) = \frac{1}{2} \left[\frac{\cos^2 \theta}{\sin^2 \theta} + \frac{\cos^2 \theta}{\theta} \right], \text{ where } \theta \text{ is the Bragg's angle. The least square linear fitting gives the precise}$$

lattice parameter as an intercept of the Y- axis as shown in Fig. 2. The lattice parameter thus determined against Zn content is shown in Fig.3 and also shown in Table 1. From the Fig. 3 it is observed that the lattice parameter increases linearly with increasing Zn content obeying Vegard's law (Vegard *et al.*, 1921).

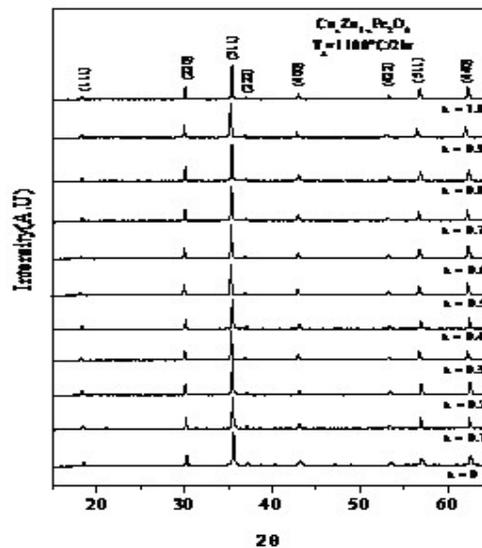


Figure 1: XRD patterns of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites

The lattice constant increases with increasing x , because the ionic radius of Co^{2+} (0.72\AA) (Patil *et al.*, 1998) is smaller than that of Zn^{2+} (0.82\AA) (Gul *et al.*, 2007). Since the radius of the substituted ions is larger than that of the displaced ions which expand the lattice and increase the lattice constant.

The dependence of bulk density d_B and X- ray density d_x upon Zn content x is represented in Fig. 4. The bulk density d_B was measured using mass and dimensional consideration

$$d_B = \frac{m}{v} = \frac{m}{\pi \cdot r^2 \cdot h}$$

where as x- ray density d_x was calculated from the molecular weight and the volume of unit cell for each sample by using the relation

$$d_x = \frac{8M}{Na^3} \text{ g/cm}^3$$

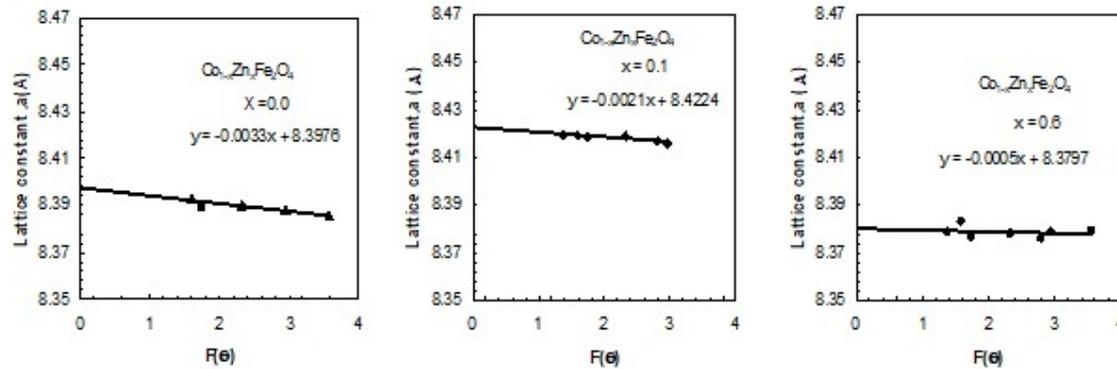


Figure 2: Variation of 'a' with F(θ) of the system $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$

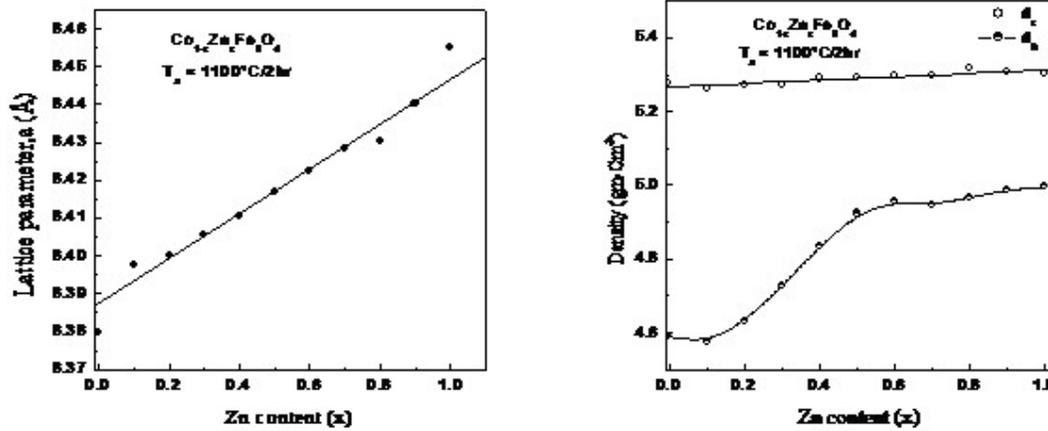


Figure 3: Variation of lattice constant 'a' as a function of Zn content (x) of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites

Figure 4: Variation of density with Zn content(x) of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites

The bulk density increases significantly with increase in Zn content. The increase of density with Zn content can be attributed to the atomic weight and density of Zn (65.37 and 7.14 gm/cm^3) which is higher than those of Co (58.9 and 8.6 gm/cm^3) respectively. The replacement of Co^{2+} by Zn^{2+} ions in the spinel leads to a variation in bonding and consequently interatomic distance and density. The oxygen ions which diffuse through the material during sintering also accelerate the densification of the material. The bulk density of the same composition reflects the same general behavior of the x-ray density d_x . The x-ray density is higher than the apparent value due to the existence of pores which depends on the sintering condition. The percentage of porosity was also calculated using the equation.

$$P = \left(1 - \frac{d_B}{d_x}\right) \times 100\%$$

Porosity changes slightly with changes of Zn content(x). It is understood from the data from Table 1 porosity values decrease significantly with increasing Zn concentration, thereby giving an observation that Zinc might be

helping in the densification of the materials. The composition $z = 0.80$ has the highest density and lowest porosity.

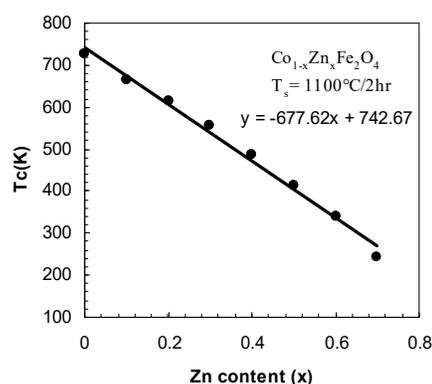


Figure 5: Variation of Curie temperature T_c with Zn content (x) of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites

In Fig.5 the variation of Curie temperature T_c as a function of Zn content of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ system. It is observed that T_c decreases continuously with the increase of Zn^{2+} content. The linear decrease of T_c is attributed to the progressive weakening the J_{AB} exchange interaction. The similar trend in the variation of T_c has been observed by some workers in Zn substituted Ni-Zn and Mg-Zn ferrites (Anjali Verma *et al.*, 2006) which is in good agreement with our experimental results. All the experimental results are shown in Table 1.

A linear dependence of T_c with Zn content is observed with $x \geq 0.7$ beyond which well defined T_c could not be determined due to complex magnetic structures and competing interactions of highly diluted composition. A linear least square fitting of T_c with x , gives an empirical relation for the whole $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ system as follows

$$T_c(x) = T_c(0) - 677.62x$$

where $T_c(0)$ is the Curie temperature of the pure Co- ferrite and $T_c(x)$ corresponds to the Curie temperature of any composition having Zn concentration x . From this empirical relation Curie temperature of Co-ferrite is found to be 742K. Our experimental results are 728K.

Table 1: Lattice parameter (a), X-ray density (d_x), bulk density (d_B), porosity(P%), Curie temperature (T_c), permeability (μ') at frequency 100KHz of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples sintered at 1100°C /2hr

Zn content (x)	a (Å)	d_x (g/cm ³)	d_B (g/cm ³)	P%	T_c (K)
0	8.3797	5.278	4.589	13	455
0.1	8.3976	5.261	4.572	13.1	390
0.2	8.4001	5.273	4.629	12.2	340
0.3	8.4086	5.261	4.725	10.2	285
0.4	8.4152	5.290	4.834	8.6	215
0.5	8.4167	5.291	4.923	6.9	140
0.6	8.4224	5.297	4.956	6.7	
0.7	8.4301	5.297	4.946	6.6	
0.8	8.4312	5.322	4.975	6.5	
0.9	8.442	5.309	4.92	7.3	
1	8.455	5.300	4.827	8.9	

4. CONCLUSIONS

The X-ray diffraction reported in the study confirmed the single phase cubic spinel structure of the prepared Co-Zn samples. The lattice constant increase with increasing Zn content obeying Vegard's law. A remarkable increase in the value of bulk density has been found with increasing Zn content. The porosity is found to decrease increase in Zn content. Curie temperatures show a decreasing trend with the successive addition of

Zn²⁺ ions. This is due to the fact that the replacement of Fe³⁺ ions by Zn²⁺ ions in the A-sites results in the decrease of strength of A–B super exchange interactions.

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