



COMPARISON STUDY OF INFLUENCE OF DOPENT ON STRUCTURAL AND MAGNETIC PROPERTIES OF NANOSTRUCTURED Co-Zn SPINEL FERRITE BY SOL-GEL AUTO COMBUSTION METHOD

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ABSTRACT:

Nanocrystalline particulates of non-magnetic doped cobalt-Zinc ferrites $\text{Co}_{0.5}\text{Zn}_x\text{M}_y\text{Fe}_{2-y}\text{O}_4$ ($x=0.5$ and $y=1$, $M \in \{\text{Al}, \text{Cr}\}$), were synthesized by using sol-gel auto combustion method. Co-, Zn-, Fe- and Al- or Cr- nitrates were the oxidizers and citric acid served as a fuel. The effect of non-magnetic content on the structural and magnetic properties has been studied. The resultant powders were sintered at 800°C for 4 hours and were characterized by XRD, FTIR and VSM. The X-ray diffraction (XRD) revealed that confirmed the formation of single phase of spinel and Lattice parameter (a), crystallite sizes (D) of VKA ferrites was smaller than that of VKC ferrite except for X-ray density (d_x). Saturation magnetization (M_s) and coercivity (H_c) of VKA ferrites was larger than that of VKC ferrite.

KEYWORDS: Ferrite, Nano particles, Sol-gel synthesis, Magnetic Property.

1. INTRODUCTION

Nanosized spinel ferrite particles, a kind of soft magnetic materials with structural formula of MFe_2O_4 are one of the most attracting a novel class of materials due to their interesting and important properties such as low melting point, high specific heating, large expansion coefficient, low saturation magnetic moment and low magnetic transition temperature [1,2] etc. Much effort are dedicated in recent years on the growth and characterizations of different cations substituted

ferrite materials prepared by several techniques due their attractive features such as chemical stability, high electrical resistivity, mechanical hardness and availability at low cost [3]. One of the important ways of modification of properties of ferrites is dependent on synthesis methods. These methods includes co-precipitation [4], hydrothermal [5], high-energy ball milling [6] and micro-emulsion [7] are developed to make Cobalt ferrite nanoparticles. Sol-gel auto combustion method has many advantages compare to other methods such as the effect of minimal contamination, processing

simplicity, low cost, high level of reactivity, easy control of the particle size and the efficiency of more homogeneous mixing of the component materials that lead to the formation of nanocrystallites. Many authors studied the effect of nonmagnetic Al or Zn or Cr substitution in the ferrite system such as NiCoMnCu [8], Co- [9], MnZn [10], CoZn [11], and Mg- [12], Ni- [13] and Ni-Mg [14]. These studies revealed that though no studies of $\text{Al}^{3+}\text{-Zn}^{2+}$ and $\text{Cr}^{+3}\text{-Zn}^{+2}$ substitution in the Co-Zn ferrite sol-gel method.

In this work, The simultaneous substitution of divalent and trivalent ions on improving the structural and magnetic properties of attempt has been made to synthesize cobalt Zinc ferrite with $\text{Al}^{3+}\text{-Zn}^{2+}$ (VKA) and $\text{Cr}^{+3}\text{-Zn}^{+2}$ (VKC) substitution with the chemical formula $\text{Co}_{0.5}\text{Zn}_x\text{M}_y\text{Fe}_{2-y}\text{O}_4$, ($x=0.5$ and $y=1$, $M \in \{\text{Al}, \text{Cr}\}$) by sol gel auto combustion method is not presented in the literature. In the present work, we report the structural and magnetic properties of cobalt Zinc ferrite nanoparticles.

2. MATERIALS AND METHOD

Nanocrystalline powders of $\text{Co}_{0.5}\text{Zn}_x\text{M}_y\text{Fe}_{2-y}\text{O}_4$ ($x=0.5$ and $y=1$, $M \in \{\text{Al}, \text{Cr}\}$), were synthesized by sol-gel auto-combustion method. AR grade citric acid ($\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$), cobalt nitrate [$\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$], Zinc nitrate [$\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$], ferric nitrate [$\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$], and Aluminum nitrate [$\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$] or chromium nitrate [$\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$] were used as starting materials. Were dissolved in distilled water to obtain a mixed solution and Adjust the pH=7 by adding ammonia [15]. The molar ratio of metal nitrates to citric acid was taken as 1:3. The obtained ferrite powders were calcined at 800°C for four hours to get the final product. X-ray diffraction patterns of the samples were Conducted on Philips X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The formation of the

spinel structure of cobalt Zinc ferrite is confirmed by X-ray diffraction analysis. The average particle size D was determined from line broadening (311) reflection using the Scherrer formula [16], $D = 0.9 \lambda / \beta \cos\Theta$, Where β is the angular line width at half maximum intensity and Θ the Bragg angle for the actual peak. FTIR spectra of all the samples were recorded in the range $400\text{--}4000 \text{ cm}^{-1}$. The saturation magnetization of sample was measured up to a maximum external field of +8 kOe, by using a vibrating sample magnetometer (VSM).

3. RESULTS AND DISCUSSION

3.1. X-RAY ANALYSIS

The XRD patterns analysed shows that samples are single-phase spinel in structure. The broad peaks in the XRD patterns indicate a fine particle nature of the particles. Fig. 1 shows the XRD pattern of $\text{Co}_{0.5}\text{Zn}_x\text{M}_y\text{Fe}_{2-y}\text{O}_4$ ($x=0.5$ and $y=1$, $M \in \{\text{Al}, \text{Cr}\}$), Co-Zn ferrite nanoparticles. The most intense peaks in all specimens, are found to match well with single-phase spinel structure.

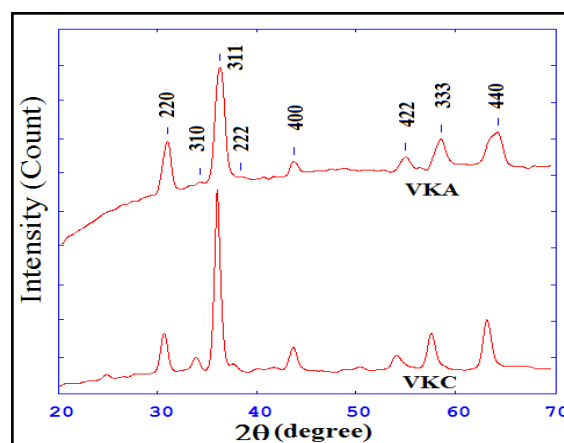


Figure.1 XRD patterns of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{AlFeO}_4$

The X-ray diffraction patterns were studied in detail to determine crystallite size by using Scherrer equation [17]. The average size distribution of powder samples estimated from X-ray peak broadening (311) diffraction peak using Scherrer formula has been found that increase from 6.900904nm (VKA) to 18.15402nm (VKC). The

grain size shows distribution with varying Cr³⁺ or Al³⁺ compositions as shown in Table 1.

Lattice constant “a” of individual composition was calculated by using the following formula: $a=d\sqrt{(h^2 + k^2 + l^2)}$, where a = lattice parameter, d = inter planar distance, hkl = miller indices.

The lattice constant obtained shows that it increasing from Co-Zn-Fe-Al (VKA) to Co-Zn-Fe-Cr (VKC) given in Table 1, can be explained on the basis of the difference in ionic radii of Fe³⁺(0.67 Å) and Cr³⁺ (0.64 Å) or Al³⁺ (0.50 Å). The replacement of Fe³⁺ with Cr³⁺ or Al³⁺ leads to shrinkage of the lattice leading to decrease of lattice constant [18]. In the present ferrite system, as per our compared study clear that in VKA, Al³⁺ (0.50 Å) ionic radii smaller than that of Cr³⁺ (0.64 Å) in VKC. Hence lattice constant VKA smaller than that of VKC.

The X-ray density of each sample was calculated using the formula [19]: $d_x = ZM / Na^3$, where Z = Number of molecules per unit cell (8), M = Molecular weight of the sample, N = Avagadro’s Number, a = lattice parameter and the obtained data are summarized in Table 1. It is obvious that, the values of X-ray density, for each sample, decreases from VKA to VKC content.

Volume of unit cell was calculated by using the formula; $V=a^3$ in (Å)³, where ‘a’ is lattice parameter. The calculated values were tabulated in Table 1. Volume of unit cell was found to increase VKA to VKC content, as it depends on lattice parameter which has increase with change in dopant content.

3.2. FTIR STUDY

FTIR spectra of Al-Zn and Cr-Zn doped cobalt Zinc ferrite were recorded in the range of 400– 4000 cm⁻¹ is as shown in fig 2. The higher frequency band (ν_1) (637-616 cm⁻¹) and lower frequency band (ν_2) (521–546 cm⁻¹) are assigned to the tetrahedral and octahedral complexes [20–21]. It explains that the normal mode of vibration of tetrahedral cluster is higher than that of octahedral cluster [22].the higher wave number ν_1 represents the vibration of Fe³⁺–O²⁻in the sublattice site A, while the lower wave number band ν_2 represents the trivalent metal oxygen vibration at the octahedral B-sites. The difference in the ν_1 and ν_2 band positions is expected because of the difference in the Fe³⁺–O²⁻distance for the octahedral and the tetrahedral sites [23]. A very weak ν_3 band is also observed for higher Al³⁺ or Cr³⁺ substituted CoZnFe₂O₄ samples ν_3 band can be assigned to the Al³⁺O²⁻ or Cr³⁺O²⁻complexes [4].Values of all the vibrational bands (ν_1 , ν_2 and ν_3) are listed in Table 1.we observed band peaks at 3440–3421 cm⁻¹(ν_4) and 1633-1629 cm⁻¹ (ν_5), which were attributed to the stretching modes and H-O-H bending vibrations of the free or absorbed water [24].

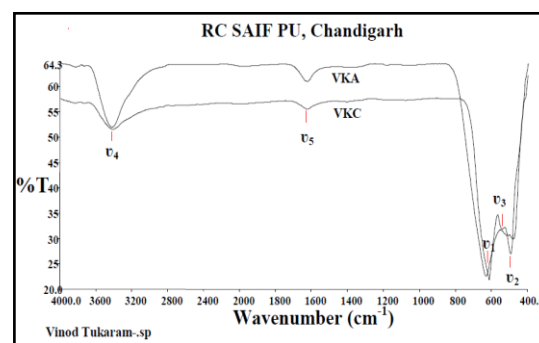


Figure. 2 FTIR patterns of Co_{0.5}Zn_xM_yFe_{2-y}O₄ (M ∈ {Al, Cr})

Table 1: Lattice constant (a), X-ray density (dx), Particle size (D), Volume of unit cell (V), IR (ν_1 and ν_2) of Co_{0.5}Zn_xM_yFe_{2-y}O₄ (x= 0.5 and y=1, M ∈ {Al, Cr}),

Samples	a (Å)	D (nm)	Dx(g/cm ³)	V	IR wavenumber		
					ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)
VKA	8.289001	6.9009	4.8742	569.516	637.26	485.3	521.3
VKC	8.376656	18.154	4.7227	587.776	616.24	496.29	546.29

3.3 MAGNETIC PROPERTIES

Fig. 3 shows the variation in saturation magnetization (M_s) for the different dopant x and y content of $\text{Co}_{0.5}\text{Zn}_x\text{M}_y\text{Fe}_{2-y}\text{O}_4$ ferrite, ($x=0.5$ and $y=1$, $M \in \{\text{Al}, \text{Cr}\}$) and the results of our measurements presented in table 2 show that the saturation magnetization with different substituted x and y content.

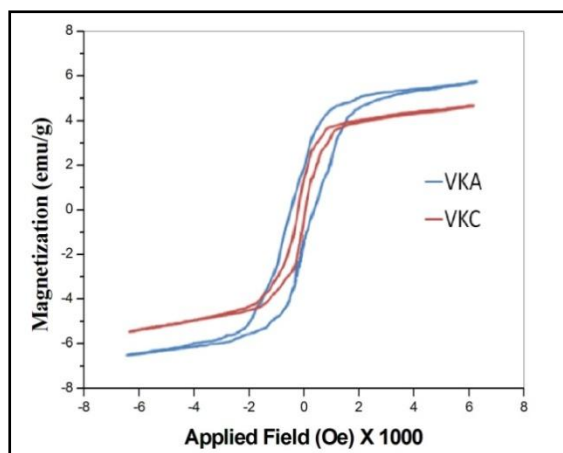


Figure. 3 Magnetization curve for VKA, VKC of $\text{Co}_{0.5}\text{Zn}_x\text{M}_y\text{Fe}_{2-y}\text{O}_4$ ($M \in \{\text{Al}, \text{Cr}\}$)

The saturation magnetization (M_s) values of the Al-Zn substituted cobalt zinc ferrite samples were found to be higher than the Cr-Zn substituted cobalt zinc ferrite, that is M_s value decreased. The value of saturation magnetization which explains that the finite size effects of the nanoparticles lead to canting or non-collinearity of spins on their surface, thereby reducing magnetization [25, 26]. The saturation magnetization decreased from VKA-VKC that is 6.3005-5.2545. The coercivity varied from 524.16 to 224.88Oe.

The coercivity values for Al-Zn substituted cobalt zinc ferrite samples were higher than the figures obtained for the same compound produced by Cr-Zn substituted cobalt zinc ferrite.

The changes in the magnetic properties of cobalt zinc ferrite can be attributed to the modification of the particle sizes, which is dependent upon the Al-Zn or Cr-Zn substituted cobalt zinc ferrite, the crystallite size of the cobalt ferrite nanoparticles changed from 6.900904nm (VKA) to 18.15402nm (VKC).

The decrease in saturation magnetization along with particle size can be attributed to the following: in the ferrimagnetic ferrite structure, the magnetization of tetrahedral sublattice is antiparallel to that of the octahedral sublattice, however, ultrafine ferrites have non collinear magnetic structure on the surface layer. The reduction in particle size causes an increase in the proportion of non-collinear magnetic structure, in which the magnetic moments are not aligned with the direction of external magnetic field. This increase in the proportion of non-collinear structure decreases the saturation magnetization.

The values of magnetic moment (n_B) for doped ferrites samples are calculated by using the formula $n_B = (M_w \times M_s) / 5585$ where M_w is the molecular weight of the composition and M_s is the saturation magnetization [27] and tabulated in Table 2.

The coercivity first higher in VKA as the reduction in particle size, reaching a value of 524.16Oe, and then decreased to 224.88 in VKC as the increase in particle size. It is reported that coercivity is affected by the factors such as magneto-crystallinity, micro strain, size distribution, anisotropy and the magnetic domain size [28–30]. In the multidomain regime, the coercivity is inversely proportional to the size of the nanoparticles [28].

Table 2: Magnetic parameters from Hysteresis loops, Saturation magnetization (Ms), Remanent magnetization (Mr), Coercivity (Hc), remanent ratio (Mr/Ms), magneton number (n_B) of $\text{Co}_{0.5}\text{Ni}_{0.5-x}\text{Zn}_x\text{Al}_y\text{Fe}_{2-y}\text{O}_4$ nanoparticles.

Samples	Ms (emu/g)	Mr (emu/g)	Hc(Oe)	(Mr/Ms)	n_B (μ_B)
VKA	6.3005	1.6726	524.16	0.265471	0.23576
VKC	5.2545	1.2816	224.88	0.243905	0.19662

4. CONCLUSIONS

The sol-gel auto-combustion technique yields nanocrystalline single phase ferrites. The simultaneous substitution of with different non-magnetic compositions has significant strong changes on the structural and magnetic properties of cobalt ferrite. The XRD pattern shows the formation of single phase spinel structure for samples. The lattice constant (a) and particle size (D) of Co-Zn-Fe-Al (VKA) nanoparticles are smaller than those of Co-Zn-Fe-Cr (VKC) except X-ray density (dx). The infrared spectra show two prominent bands corresponding to the spinel ferrite phase. Magnetic measurements through VSM indicated the saturation magnetization (M_s),

coercivity (Hc) and magnetic moment (n_B) of (VKA) nanoparticles are larger than those of (VKC) nanoparticles.

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