

Characterization of Chromium Substituted Cobalt Nano Ferrites Synthesized by Citrate-Gel Auto Combustion Method

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ABSTRACT

Co-Cr nano-ferrites, having the chemical formula $\text{CoCr}_x\text{Fe}_{2-x}O_4$ (where x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0), were synthesized by the Citrate-gel auto combustion method. Synthesized powders were sintered at 500°C for 4 hours in an air and were characterized by XRD, SEM and EDS. XRD analysis showed cubic spinel structure of the ferrites and the crystallite sizes (D) were found in the range of 6 - 12 nm. The values of lattice parameter (a) decreased and X-ray density (d_x) increased with the increase of Cr content. Scanning Electron Microscopic (SEM) studies revealed nano crystalline nature of the samples. An elemental composition of the samples was studied by Energy Dispersive Spectroscopy (EDS). The observed results can be explained on the basis of composition and crystal size.

Keywords: Co-Cr Nano-Ferrites; Citrate-Gel Auto Combustion; X-Ray Diffraction; SEM; EDS

1. Introduction

Spinel ferrites are commercially important materials due to their excellent magnetic and electrical properties [1]. The interesting physical and chemical properties of the ferrites arise from their ability to distribute the cations among the tetrahedral (A) and octahedral (B) sites [2]. Among the various ferrites, cobalt ferrites have received recent attention as they possess excellent chemical stability, good mechanical hardness, remarkably high electrical resistivity, and large permeability at high frequency and cost effectiveness [3,4]. Due to these properties, cobalt ferrites have been extensively used in electronic devices [3,4], Magnetic Resonance Imaging (MRI), Target drug delivery, Hyperthermia for cancer treatment [5,6], high density storage devices, magnetic fluids [7,8], transformer cores, microwave devices, humidity and gas sensors, etc. Substitution of elements such as Chromium into Cobalt ferrites has been proposed, in order to tailor the magnetic and magneto mechanical properties of these materials [9]. Chromium substituted Cobalt ferrites are of particular interest in which the Cr⁺³ ions are reported to have a strong preference for the B sites (Octahedral) of the spinel structure of the ferrites [10,11]. A few previous

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investigations regarding Chromium substituted Cobalt ferrites have been reported which mainly concentrated on the Chromium rich side (1 < x < 2) [12,13]. It is known that the properties of the ferrites depend strongly on their composition and micro structure which are sensitive to the processing methods used to synthesize them. Several methods have been reported to synthesize chromium substituted Cobalt ferrite nano-materials; these include Powder Ceramic technique [14], Micro-emulsion method [15], Chemical Co-precipitation method [16] and Soft citrate gel method [17]. To the best of my knowledge, a little information is available on nano sized Chromium substituted Cobalt ferrites synthesized by Citrate-gel. Auto combustion method, which is a simple process, speeds up the synthesis and offers a significant saving in time, energy consumption over traditional methods. Hence in the present study we preferred the Citrate Gel auto combustion method for the synthesis of Chromium substituted Cobalt nano-ferrites.

2. Experimental

2.1. Synthesis

A series of Chromium substituted Cobalt nano ferrites

having the chemical formula $CoCr_xFe_{2-x}O_4$ (where x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) were prepared by Citrate Gel Auto-combustion method. The starting materials were Cobalt Nitrate (Co(NO₃)₂·6H₂O), Ferric Nitrate (Fe (NO₃)₂·9H₂O), Chromium Nitrate (Cr(NO₃)₂·9H₂O), Citric acid (C₆H₈O₇·H₂O) and Ammonia (NH₃) all of 99% pure AR grade. Calculated quantities of metal nitrates were dissolved together in a minimum amount of distilled water to get clear solution. An aqueous solution of Citric Acid was then added to the metal nitrate solution. The molar ratio of Citric acid to the total moles of nitrate ions was adjusted to 1:3. The mixture was stirred to obtain a homogeneous solution and then was slowly heated to 80°C at a rate of 5°C/minute using a hot plate magnetic stirrer. P^{H} of the solution was adjusted to 7 by adding Ammonia (NH₃) solution. A Sol is formed. The resulting solution was evaporated to dryness by heating at about 150°C on a hot plate with continuous stirring. As a result the viscosity rose due to cross linking of carboxylatometal complexes into a three dimensional structure (pierre et al., 1990; Jang et al., 1995, Narebder abd Messing, 1997) and get started to form a viscous gel (Figure 1(a)). When finally all water molecules were removed from the mixture by increasing the temperature to 200°C, the viscous gel began frothing. The gel gave a fast flameless auto combustion reaction with the evolution of large amounts of gases (Figure 1(b)). It started in the hottest zones (Figure 1(c)) of the beaker and propagated from the bottom to the top like the eruption of a Volcano (Figure 1(d)). The reaction was completed in a minute giving rise to dark grey voluminous product with a structure similar to Branched tree (Figure 1(e)). Finally the burnt powder was ground and was calcined in air at temperature 500°C for four hours to obtain a spinel phase.

2.2. Characterization

X-ray Diffraction with Cuk α (lambda = 1.54 Å) was used to study the single phase nature and nano-phase formation of the Co-Cr ferrite system at room temperature by continuous scanning in the range of 2°C to 85°C.

Micro structural analysis of the prepared samples was carried out by scanning Electron microscopy (SEM) and elemental compositional analysis for all samples was done by Energy Dispersive Spectroscopy (EDS).

3. Results and Discussions

3.1. XRD Analysis

The X-ray diffraction patterns of all the samples were shown in **Figure 2**. XRD patterns and the crystalline phases were identified by comparison with reference data from the ICSD card No. 22-1086 for Cobalt ferrites $(CoFe_2O_4)$. The XRD patterns of all the Chromium sub-



Figure 1. (a) Viscous gel formation; (b) Self ignition; (c) Combustion of the mixture; (d) Propagation of combustion like volcanic eruption; (e) Dark grey voluminous product with a structure similar to a branched tree.

stituted Cobalt ferrites showed a homogeneous single phased cubic spinel belonging to the space group Fd3m (confirmed by ICSD Ref 22-1086). All the Braggs reflections have been indexed, which confirmed the formation of a well defined single phase cubic spinel structure without any impurity peaks. All the peaks are allowed peaks. The strongest reflection has come from (311) plane that indicates spinel phase.

Crystallite size of each sample was calculated from Scherrers Formula [18] mentioned below by using high intensity peak (311).

$$D = \frac{0.91\lambda}{\beta\cos\theta}$$

where λ = Wavelength of X-ray, β = Full width and Half Maxima in radians, θ = Bragg's angle at the peak position.

Measured crystallite size was in the range of 6 - 12 nm (shown in **Table 1**) for different compositions with a significant increase of 6 nm in response to the increase in Cr substitution. To my knowledge Citrate-gel method is the only method which has resulted in Co-Cr ferrites with such a very small crystallite size.

Lattice parameter "*a*" of individual composition was calculated by using the following formula and values were tabulated in **Table 1**.

$$a = d\sqrt{h^2 + k^2 + l^2}$$



Figure 2. XRD patterns of $CoCr_xFe_{2-x}O_4$ nano ferrite (where x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0).

Table 1. Crystallite size (D), Lattice parameter (a) of $Co-Cr_xFe_{2-x}O_4$ Nano-ferrites with x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0.

Ferrite composition	Crystallite size (nm)	Lattice parameter (Å)		
CoFe ₂ O ₄	6.5	8.390		
CoCr _{0.1} Fe _{1.9} O ₄	12.1	8.380		
$CoCr_{0.3}Fe_{1.7}O_4$	12.8	8.367		
CoCr _{0.5} Fe _{1.5} O ₄	11.9	8.356		
$CoCr_{0.7}Fe_{1.3}O_4$	10.5	8.346		
$CoCr_{0.9}Fe_{1.1}O_4$	10.7	8.335		
CoCrFeO ₄	12.3	8.330		

where a = lattice parameter, d = inter planar distance, hkl = miller indices.

The variation of lattice parameter with Cr⁺³ compositions was shown in **Figure 3**. The lattice parameter was found to decrease linearly with increasing Cr concentration. This linear variation indicates that the Co-Cr ferrite system obeys Vegard's law [19].

A similar behavior of lattice parameter with dopant concentration was observed by several investigators in various ferrite systems [20,21]. The decrease in lattice parameter with increase in Cr^{+3} content can be explained on the basis of relative ionic radii of Cr^{+3} and Fe^{+3} ions.

As Cr^{+3} ions have small ionic radii (0.63 Å) than that of Fe^{+3} (0.64 Å), a partial replacement of Fe^{+3} ions by Cr^{+3} ions results in a decrease in lattice parameter. Calculated lattice parameter for Cobalt ferrite (CoFe₂O₄) was in good agreement with the standard value (8.391 Å) reported from ICSD data.

X-ray density (d_x) for different compositions was calculated using the formula [22] and calculated values were tabulated in **Table 2**.

$$d_x = \frac{ZM}{Na^3} gm/cc$$

where Z = Number of molecules per unit cell (8), M = Molecular weight of the sample, N = Avagadro's Number, a = lattice parameter.

The variation of X-ray density with Cr^{+3} compositions was shown in **Figure 4**. X-ray density depends on the lattice parameter and molecular weight of the sample. In the present Co-Cr system with increase in the Cr^{+3} content, it is observed that the molecular weight is decreased (due to greater atomic weight of Fe-55.847 gm/mole and less atomic weight of Cr-51.996 gm/mole) and the lattice



Figure 3. Variation of lattice parameter with Cr composition for Co-Cr nano ferrites.

Table 2. X-ray density (d_x) , volume of the unit cell (V) of-CoCr_xFe_{2-x}O₄ nano-ferrites with x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0.

Ferrite composition	Density d_x (gm/cc)	Volume of unit cell (V)		
CoFe ₂ O ₄	5.276	590		
CoCr _{0.1} Fe _{1.9} O ₄	5.287	588		
CoCr _{0.3} Fe _{1.7} O ₄	5.294	585		
CoCr _{0.5} Fe _{1.5} O ₄	5.297	583		
CoCr _{0.7} Fe _{1.3} O ₄	5.299	581		
CoCr _{0.9} Fe _{1.1} O ₄	5.302	579		
CoCrFeO ₄	5.303	578		



Figure 4. Variation of X-ray density with Cr composition for Co-Cr Nano ferrites.

parameter has also decreased. X-ray density was found to increase with increasing Cr concentration this is due to the fact that decrease in volume (V) of the unit cell overtakes the decrease in mass (M) in the system.

A similar behavior of X-ray density with Cr composition was reported by Md. Javed Iqbal, Mah Rukh Siddiqyah in Co-Cr ferrite system synthesized by Microemulsion method [15].

Volume of unit cell was calculated by using the formula

$$V = a^3 in \left(\text{\AA} \right)^3$$

where 'a' is lattice parameter.

The calculated values were tabulated in **Table 2**. Variation of Volume of unit cell with Cr Composition was shown in **Figure 5**. Volume of unit cell was found to decrease with increase in Cr content, as it depends on lattice parameter which has decreased with increase in Cr content.

X-ray density(d_x), volume of the unit cell (V) of CoFe₂O₄ were in good agreement with the standard values (5.274 gm/cc, 590.99(A⁰)³) from ICSD data.

The distance between magnetic ions (hopping length) in A site (tetrahedral) and B site (octahedral) were calculated using the relations

$$d_A = 0.25a\sqrt{3}, d_B = 0.25a\sqrt{2}$$

"a" = lattice parameter.

The calculated values of the hopping length for Tetrahedral site(d_A) and octahedral(d_B) of different compositions were tabulated in **Table 3**. The relation between hopping length for Octahedral and Tetrahedral sites as a function of Cr⁺³ content(x) was shown in **Figure 6**. It is observed that the hopping length decreases as the Cr content increases. It may be due to the fact that Cr⁺³ ion has smaller radius (0.63 Å) than Fe⁺³ ion *i.e.* (0.64 Å).

This makes the magnetic ions become closer to each other and hopping length decreases.



Figure 5. Variation of volume of the unit cell with Cr compositionfor Co-Cr nano ferrites.



Figure 6. Variation of hopping length d_A and d_B of Co Cr_x Fe_{2-x}O₄ with x= 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0.

Table 3. Values of hopping length d_A and d_B of Co Cr_x Fe_{2-x}O₄ with x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0.

Ferrite composition	d_A	d_B
CoFe ₂ O ₄	3.6329	2.9659
CoCr _{0.1} Fe _{1.9} O ₄	3.6285	2.9623
CoCr _{0.3} Fe _{1.7} O ₄	3.6229	2.9577
$CoCr_{0.5}Fe_{1.5}O_4$	3.6181	2.9538
$CoCr_{0.7}Fe_{1.3}O_4$	3.6138	2.9503
$CoCr_{0.9}Fe_{1.1}O_4$	3.6090	2.9464
CoCrFeO ₄	3.6069	2.9446

Similar behavior of hopping length with Cr⁺³ composition was observed for the Mg-Cr system synthesized by double sintering technique reported by V.B. Kawade, G.K. Bichile, K.M. Jadhav [21].

3.2. Morphology by SEM

Morphology of the prepared samples by Citrate-gel method was studied using scanning electron microscope (SEM) where the secondary electron images were taken at different magnifications to study the morphology. The scanning electron microscopic images of all the synthesized samples were shown in **Figure 7**.

The images show that the particles have an almost homogeneous distribution, and some of them are in agglomerated form. It is evidenced by SEM images that the aggregation of particles lies in nanometric region. The particles were observed as uniform grains (in different SEM images) confirming the crystalline structure of Co-Cr ferrites which were detected by XRD studies. The formation of Fe₂O₄ was chemically favored by heating during the synthesis where as final reaction was completed during the sintering where the pores between the particles were removed combined with growth and strong bonds by agglomeration. It is also observed that agglomeration of the compound was increased with change in composition of the sample from x = 0 to x = 1 which may be due to the Cr⁺³ ions. SEM images reveal that with increase in Cr composition the grain size has increased (x = 0 to x = 1), hence is an evidence for XRD analysis.

3.3. Elemental Analysis by EDS

The elemental analysis of all the Co-Cr nano ferrite samples with different compositions was analyzed by Energy Dispersive Spectrometer (EDS) and the elemental % and atomic % of different elements in the were shown in the **Table 4**. The EDS pattern for samples with x = 0.0, 0.1 and 0.5 were shown in **Figure 8** which indicates the elemental and atomic composition in the sample. The compounds show the presence of Co, Cr, Fe and O without precipitating cations.



x=0.0





Figure 7. SEM images of Co Cr_x Fe_{2-x}O₄ with x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0.





Element	О		Fe		Со		Cr	
Ferrite composition	Element%	Atomic %	Element %	Atomic %	Element %	Atomic %	Element %	Atomic %
CoFe ₂ O ₄	19.93	47.18	37.89	25.7	42.18	27.12	-	-
$CoCr_{0.1}Fe_{1.9}O_4$	44.25	73.44	18.91	8.99	20.61	9.29	16.23	8.29
CoCr _{0.3} Fe _{1.7} O ₄	34.99	65.22	20.84	11.13	24.87	12.58	19.3	11.07
CoCr _{0.5} Fe _{1.5} O ₄	22.44	50.17	25.97	16.63	28.12	17.06	23.47	16.14
CoCr _{0.7} Fe _{1.3} O ₄	27.02	56.34	23.51	14.04	27.9	15.79	21.56	13.83
$CoCr_{0.9}Fe_{1.1}O_4$	13.07	34.31	26.86	20.2	31.95	22.77	28.12	22.72
CoCrFeO ₄	34.16	64.36	21.3	11.5	24.63	12.6	19.91	11.54

4. Conclusions

- Citrate Gel auto combustion technique is a convenient way for obtaining a homogeneous nano sized mixed Co-Cr ferrites. The process involves no impurity pickup and material loss. It is a very simple and economical method where no specific heating or cooling rate is required. It is a low temperature processing technique and requires shorter sintering duration.
- X-ray diffraction pattern confirms the formation of cubic spinel structure in single phase without any impurity peak. It is in good agreement with the standard data from ICSD.
- The crystallite size of the various Co-Cr ferrites was in the range of 6 12 nm.
- The lattice parameter has decreased with the increase of Cr substitution in Co-Cr ferrites which indicate that the mixed Co-Cr ferrite system obeys the Vegard's law.
- SEM micrographs of various compositions indicate the morphology of the particles is similar. They reveal largely agglomerated, well defined nano particles of the sample powder with inhomogeneous broader grain size distribution.
- EDS data give the elemental % and atomic % in the mixed Co-Cr ferrites and it shows the presence of Co, Cr, Fe and O without precipitating cations.

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REFERENCES

- P. V. Reddy and T. S. Rao, "Dielectric Behavior of Mixed Li-Ni Ferrites at Low Frequencies," *Journal of Less Common Metals*, Vol. 86, 1982, pp. 255-261. doi:10.1016/0022-5088(82)90211-9
- [2] G. Blasse, *Philips Research Reports*, Suppl. 3, 1964.
- [3] J. Smit and H. P. J. Wijn, "Ferrites," Philips Technical Library, Eindhoven, 1959.
- [4] K. Ishino and Y. Narumiya, "Development of Magnetic Ferrites: Control and Application of Losses," *American Ceramic Society Bulletin*, Vol. 66, No. 10, 1987, pp. 1469-1474.
- [5] D. H. Kim, S. H. Lee, K. N. Kim, K. M. Kim, I. B. Shin

- [6] S. Somiya, S. Aldinger, N. Claussen, R. M. Uchino, R. M. Uchino, K. Koumto and K. Kanenoin, "Handbook of Advanced Ceramics, Vol. II, Processing and Their Applications," Elsevier Academic Press, Waltham, 2003, p. 394.
- [7] F. Zhang, S. Kantake, Y. Kitamoto and M. Abe, "Spin-Spray Ferrite-Plated co Ferrite Films with High Coercivity for Perpendicular Magnetic Recording Media," *IEEE Transactions on Magnetics*, Vol. 35, No. 5, 1999, pp. 2751-2753. doi:10.1109/20.800974
- [8] R. Arulmurugan, G. Vaidyanathan, S. Sendhilnathan and B. Jeyadavan, "Mn Zn Ferrite Nanoparticles for Ferrofluid Preparation: Study on Thermal-Magnetic Properties," *Journal of Magnetism and Magnetic Materials*, Vol. 298, No. 2, 2006, pp. 83-94. doi:10.1016/j.jmmm.2005.03.002
- [9] J. A. Paulsen, A. P. Ring, C. C. HLO, J. E. Snyder and D. C. Jiles, "Manganese-Substituted Cobalt Ferrite Magnetostrictive Materials for Magnetic Stress Sensor Applications," *Journal of Applied Physics*, Vol. 97, No. 4, 2005, Article ID: 044552. doi:10.1063/1.1839633
- [10] R. C. O. Handley, "Modern Magnetic Materials Principles and Applications," Wiley, New York, 2000.
- [11] A. Hauet, J. Teillet, B. Hannoyer and M. Lenglet, "Mössbauer Study of Co and Ni Ferrichromites," *Physics Status Solidi* A, Vol. 103, No. 1, 1987, pp. 257-261. doi:10.1002/pssa.2211030129
- [12] L. G. Antoshina, A. N. Goryaga and R. R. Annarv, "Magnetization Processes of the Sample CoFeCrO₄ with Frustrated Magnetic Structure," *Journal of Magnetism and Magnetic Materials*, Vol. 195, No. 3, 1999, pp. 608-610. doi:10.1016/S0304-8853(99)00230-9
- [13] T. Tsushima, "Magnetic Properties of Ferrite-Chromite Series of Nickel and Cobalt," *Journal of Physics Society* of Japan, Vol. 18, 1963, pp. 1162-1166. doi:10.1143/JPSJ.18.1162
- [14] K. Krieble, C. C. H. Lo, Y. Melikhov and J. E. Snyder, "Investigation of Cr Substitution in Co Ferrite (Co-Cr_xFe_{2-x}O₄) Using Mossbauer Spectroscopy," *Journal of Applied Physics*, Vol. 99, No. 8, 2006, Article ID: 08M912. doi:10.1063/1.2167051
- [15] M. J. Iqbal and M. R. Siddiquah, "Electrical and Magnetic Properties of Chromium Substituted Cobalt Ferrite Nano Materials," *Journal of Alloys and Compounds*, Vol. 453, No. 1-2, 2008, pp. 513-518. doi:10.1016/j.jallcom.2007.06.105
- [16] M. Anis-ur-Rehman, M. Ansari, Z. N. Mughal, M. S. Awan and A. Maqsood, "Synthesis and Thermoelectric Studies in Cr doped Cobalt Ferrite Nano Paticles," *Key Engineering Materials, Advanced Materials XII*, Vol. 510-511, 2012, pp. 171-176. doi:10.4028/www.scientific.net/KEM.510-511.171
- [17] P. P. Hankare, U. B. Sankpal, R. P. Patel, P. D. Lokhande and R. Sasikala, "Synthesis, Characterization and Catalytic Activity of Chromium Substituted Cobalt Ferro

Spinels," *Materials Science and Engineering*: *B*, Vol. 176, No. 2, 2011, pp. 103-109. doi:10.1016/j.mseb.2010.10.005

- [18] B. D. Cullity, "Elements of XR-Diffraction," Addison Weseley Publishing, Reading, 1959, p. 132.
- [19] L. Vegard, "The Constitution of Mixed Crystals and the Space Occupied by Atoms," *Zeitsch rift für Physics*, Vol. 5, No. 17, 1921, pp.17-23.
- [20] V. B. Kawade, G. K. Bichile and K. M. Jadhav, "X-Ray and Infrared Studies of Chromium Substituted Magnesium Ferrite," *Material Letters*, Vol. 42, No. 1-2, 2000,

pp. 33-37. doi:10.1016/S0167-577X(99)00155-X

- [21] R. Arulmurugan, B. Jeyadevan, G. Vaidyanathan and S. Sendhilnathan, "Effect of Zinc Substitution on Co-Zn and Mn-Zn Ferrite Nanoparticles Prepared by Coprecipitation," *Journal of Magnetism and Magnetic Materials*, Vol. 288, 2005, pp. 470-477. doi:10.1016/j.jmmm.2004.09.138
- [22] R. C. kumbale, P. A. sheikh, S. S. Kamble and Y. D. kolekar, "Effect of Cobalt Substitution on Structural Magnetic and Electric Properties of Nickel Ferrite," *Journal of Alloys and Compounds*, Vol. 478, No. 1-2, 2009, pp. 599-603. doi:10.1016/j.jmmm.2005.03.007