INTERNATIONAL JOURNAL FOR INNOVATIVE RESEARCH IN MULTIDISCIPLINARY FIELD ISSN: 2455-0620 Volume - 6, Issue - 5, May – 2020
Monthly, Peer-Reviewed, Refereed, Indexed Journal with IC Value: 86.87 Impact Factor: 6.497
Received Date: 28/04/2020 Acceptance Date: 10/05/2020 Publication Date: 31/05/2020

Effect of Co $^{3+}$ ion substitution on structural, electrical and electromagnetic characterization of calcium ceramics synthesized by sol-gel auto combustion route

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Abstract: *M-type Calcium hexaferrite substituted with Cobalt ions compounds were successfully synthesized by sol-gel auto combustion route with general chemical formula $CaFe_{12-x}Co_xO_{19}$ (where $0 \leq x \leq 4$). Their structural,electrical and magnetic properties are studied and reported. The structural properties are characterized by X-ray diffractometer and SEM. The X-ray diffraction data of all the samples have confirmed the formation of single-phase M-type hexagonal ferrites with the space group of $P6_3/mmc$. Also, an electrical resistivity was measured by using two probe technique. Magnetic properties are studied with the help of vibrating sample magnetometer (VSM). Saturation magnetisation, remanent magnetisation, Coercive field are calculated and reported. Results of VSM studies show the increase in saturation magnetization with the substitution.*

Key Words: *M Type Hexaferrite, X-Ray diffraction (XRD), Retentivity (Mr), Coercivity (Hc) and Saturation Magnetization (Ms)*

1. INTRODUCTION:

Ferrites continued to attract more attention of researchers over the years due to their broad category of applications over wide frequency range, low cost and high performance. They are found suitable in microwave devices, memory core, perpendicular magnetic recording and permanent magnets. These applications need significant magnetic and electrical specifications and in this view, several attempts have been made to modify the properties of hexagonal ferrites using different processing route including external doping [1- 4]. Recently the research on ferrite have been shifted towards developing ferrites at nanometric scale due to its unique mechanical, electrical, optical and magnetic properties. The unique property of nanostructure materials are due to changed electronic structure closed to that of isolated atom or molecule. Hexagonal ferrites are a large family of ferrimagnetic materials. Among these, M-type hexaferrites are the most popular due to their large applications as permanent magnets. Substituted hexaferrites belong to M-Type with general formula MFe12O19 where M is usually barium, strontium, Calcium or Lead, are of the significant attractions for researchers because of their applications in the field of material science as permanent magnets, microwave devices so on and so forth [5]. The basic structure is hexagonal with all 38 oxygen ions occupying the interstitial sites forming a close packed assembly. 24 ferric ions occupy five different locations in the unit cell such as 2a, 2b, 4f1, 4f2 and 12k, where 2a, 4f2 and 12k are octahedral, 4f1 is tetrahedral and 2b is bi-pyramidal sites. The magnetic nature of magnetoplumbites is determined by the substituted trivalent ions for ferric ions, which occupy different sites in the structure [6-10]. The Fe^{+3} ions when replaced partially by other trivalent metal ions, the magnetic properties of the calcium ferrite undergo changes [11,12]. To prepare Hexagonal ferrites,various synthesis methods like chemical co-precipitation, hydrothermal, sol-gel, combustion [13-17] etc. have been developed. In the present work, Calcium hexaferrites sbstituted with trivalent Co ions synthesized by combustion method are studied and reported.

2. MATERIALS AND EXPERIMENTAL METHOD:

Calcium M-type hexaferrites having chemical formula $CaFe_{12-x}Co_xO_{19}$ are synthesized by taking stoichiometric amounts of reactive nitrates $Ca(NO_3)_2$, $Fe(NO_3)_2.9H_2O$, $Co(NO_3)_2.6H_2O$. The nitrates are dissolved completely into 100 ml distilled water at 50 ^{0}C for 20-30 min to obtain aqueous solution. Urea is used as fuel which gives required energy to initiate exothermic reaction. The viscous gel produced is then kept for an hour in the room temperature and then the combustion is carried in microwave oven for 15-20 min. The combustion takes place in self-propagating manner and the gel gets converted into reddish-brown voluminous fluffy porous product which will then crushed to get fine homogeneous powder. The powder is then sintered by giving moderate heat treatments. The sintering is done at 800 ^{O}C for 2 hours by sequentially increasing and decreasing temperature at the rate of 4^{o}C/min to remove unwanted traces if present. Calcium hexaferrites substituted with trivalent Co^{+3} ions with general chemical formula $CaFe_{12-x}Co_xO_{19}$ ($0 \le x \le 4$) have been synthesized successfully by sol-gel auto combustion technique. Samples were prepared with AR grade calcium nitrate, iron nitrate and Cobalt nitrate. Urea ODH ($C_2H_6N_4O_2$) was used as fuel. All Samples were calcinated at 900°C for 4 hours and allowed to cool gradually at rate of 5 degree per minute.

The structural characterization of the samples was performed by Philips X-ray diffractometer with Cu-Ka radiation (λ=1.5405Å) in the 2θ range of 10-120, in angular steps of 0.02°.The average particle size D, was determined from line broadening of (107) reflection using Scherrer formula given by

$$D = k\lambda/h\cos\theta$$

where D is average size of the crystallites, k is Scherer constant (0.9), λ is wavelength of radiation (1.54056Å) and h is peak width of half height (FWHM).Values of lattice constant 'a' and 'c' and unit cell volume 'V' were calculated by using following equations and are given in table 1. The morphology and size of the particles were studied using SEM (fig. 2.) The particle size of each sample was analysed from the SEM images with the help of Image J software and the values are found to be in comparable with calculated values. The measurement of electrical conductivity by using two-terminal method was employed . The measurements were taken in the range from 150 °C to 850 °C. Finally graphs of ln σ against 1/T were plotted and from the slope of these graphs the activation energies for the compounds were calculated using the relation,

$$\Delta E = 8.617 \times 10^{-5} [\ \Delta(\ln(1/\sigma) / \Delta(1/T)\ ]$$

Also, Seeback coefficient measurements were carried out using two-probe set up fabricated in the laboratory. The measurements were taken in the temperature range 350°K to 450°K. The type of carriers responsible for conduction was determined in each of the compound from these studies. In order to prepare pellet for the above observations the compound prepared was grounded to fine particle size in an agate mortar. The powder was mixed with 5% polyvinyl acetate solution made in A.R. grade acetone, as binder and mixed thoroughly. This mass was then transferred to a die and pressed under pressure of 5 tons per cm^2 using a hydraulic press. The pellets so prepared were then heated in a furnace up to 500 °C to remove the binder. After maintaining this temperature for few hours the pellets were slowly cooled to room temperature. In this way crack free pellets in the shape of a cylinder of small height were obtained. The end faces of the pellets, so prepared, were gently grounded over zero number sand paper to ensure smooth surfaces. The dimensions of the pellets were measured accurately. The smooth and flat parallel faces of the pellets were coated with uniform thin layer of silver paste to facilitate a good electrical contact with the electrodes. The silver paste was dried by heating the pellet slowly for few hours in air at 500 °C. The thin coating of silver paste thus formed was adherent and chemically inert. Pellets were stored in desiccators if found necessary. The magnetic properties were studied using vibrating sample magnetometer at room temperature. Applying the field in the range of -20 K - +20 K, carried out measurements. Saturation magnetization, Coercive field and Remanent magnetization were calculated and reported (Table 2).

3. RESULTS AND DISCUSSION:

3.1: Structural analysis: Investigated ferrite sample $Ca\ Fe_{12-x}Co_xO_{19}$ powder synthesized by sol-gel auto combustion technique correspond to M-type calcium hexaferrite structure as shown fig(1). X-ray diffraction pattern of $Ca\ Fe_{12-x}Co_xO_{19}$ hexagonal ferrite under investigation were obtained using X-ray diffractometer. The hexagonal M-structure with space group ($P6_3/mmc$) (No. 194), which confirms that phase belongs to magnetoplumbite indicating that the crystal structure were single phase hexagonal magnetoplumbite after substitution with Co^{3+} ions respectively. The lattice constant a and c of hexagonal calcium ferrite were calculated using equation (1)

$$\frac{1}{d^2} = \frac{4h^2 + k^2k + hk}{3a^2} + \frac{l^2}{c^2}$$

Where h ,k, l are miller indices, d is interplaner distance. The lattice parameter a and c found to be 6.023 to 6.055 (Å) and 22.304 to 21.629 (Å) respectively. There is a small shift in the peak position with the increase of substituting ion. This is due to the small ionic radius of Co^{+3} (0.61 Å) compared to the ionic radius of Fe^{+3} (0.65 Å). Structural parameters of the samples are given in table 1. There is a variation in the particle size with substitution. Volume of the cell also slightly decreases with the increase in substitution.

XRD spectrum of Ca $Fe_{12-x}Co_xO_{19}$

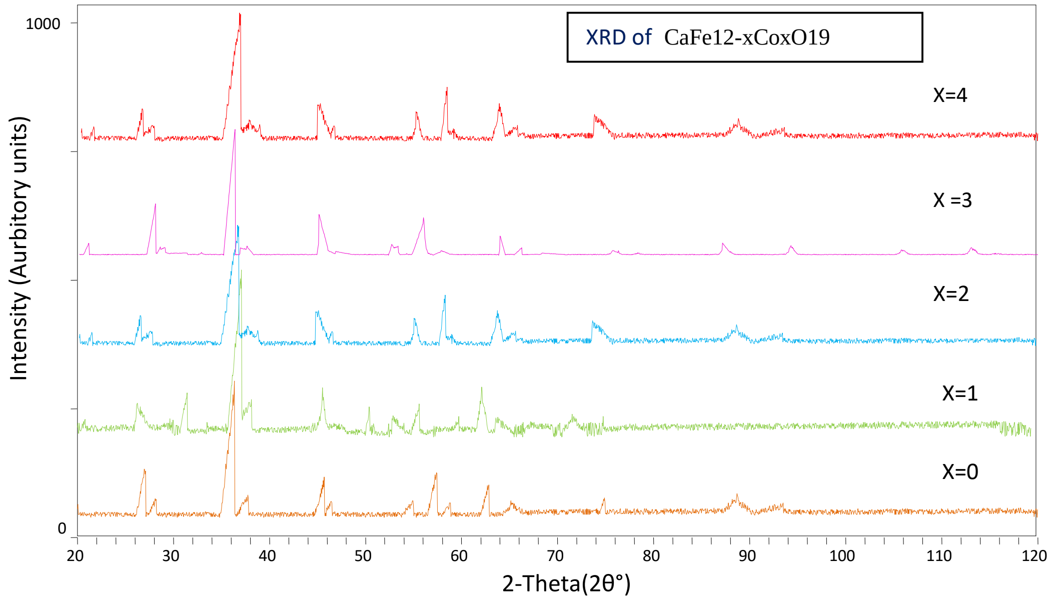


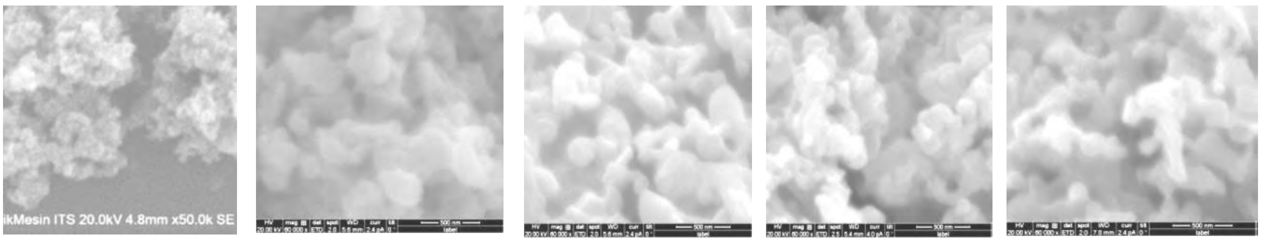
Figure. 1: XRD spectrum of Ca $Fe_{12-x}Co_xO_{19}$

Table 1: Consolidated structural data of Ca $Fe_{12-x}Co_xO_{19}$

Sample Ca $Fe_{12-x}Co_xO_{19}$	D (nm)	*a* (Å)	c (Å)	V (Å3)
X=0	29	6.023	22.304	699.868
X=1	27	6.036	22.096	697.687
X=2	13	6.044	21.979	695.932
X=3	17	6.050	21.724	690.378
X=4	24	6.055	21.629	686.237

3.2: Microstructure analysis: The SEM images of the samples are shows in figure-2 . From the figures it is evident that particles are in Nano size and almost spherical in shape.

SEM images of Ca $Fe_{12-x}Co_xO_{19}$ (x=0,1,2,3,4)



(a) x=0 (b) x=1 (c) x=2 (d) x=3 (e) x=4

Figure 2: SEM Images of Ca $Fe_{12-x}Co_xO_{19}$ (x=0,1,2,3,4)

3.3: Electrical Studies: In this present work, the observed value of electrical conductivity, activation energy for specimens are tabulated in table – 2

Table – 2: Electrical conductivity of Ca $Fe_{12-x}Co_xO_{19}$ **ferrites**

Compounds	Electrical Resistivity at room temperature(Ω cm)	Activation energy E in (ev)	Electrical Conductivity at room temperature. $(\Omega\ cm)^{-1}$
$CaFe_{12}O_{19}$	4.559x10 11	0.77	2.193 x10 -12
$CaFe_{11}\ Co\ O_{19}$	3.21x 10 9	0.63	3.11 x10 -10
$CaFe_{10}Co_2O_{19}$	4.65x10 7	0.52	2.148 x10 -8
$CaFe_9\ Co_3\ O_{19}$	6.84x10 6	0.48	1.46 x10 -7
$CaFe_8\ Co_4\ O_{19}$	1.72x10 5	0.39	5.78 x10 -6

The plot of $\ln \sigma$ vs (1/ T) x 10^{-3} K for the entire sample was almost linear. The electrical conductivity of these ferrites increases with increasing ferrite ion concentration. The electrical conductivity of sintered specimens varies from to 2.193 x10^{12} Ω^{-1} cm to 5.78 x10^{-6} Ω^{-1} cm of these ferrites. The other workers have obtained a conductivity value of 2 x10^{-2} Ω^{-1}cm for calcium ferrite that obtained is 2.3 x 10^{-6} Ω^{-1} cm [21]. The electrical conductivity value obtained for the compounds are 2.193 x 10^{-12} to 5.78 x 10^{-6} Ω^{-1} cm. The value of the conductivity may be partly attributed to the low evaporation of calcium from the sample prepared different from these of Rozlescu etal 1974 and Venugopal Reddy 1981.The variation of activation energy with the substitutional variable parameters x -may be explain on the basis of Vewrway model [22-24], a small number of ferrous ions (Fe^{+2}) are generally developed during sintering process which lead the conductivity in ferrites suggesting the hopping mechanism according (Fe^{+2}-Fe^{+3}+e^-) [25]. However these transition take place for a very small interval of time and are not detectable by the ordinary method .This valence exchange mechanism of Verwey may be considered for these ferrites as general applicable to M-type ferrite.

3.4: Magnetic studies: The hysteresis B-H curve measurements were carried out at room temperature, coeresivity (Hc), retentivity (Re),saturation magnetization (Ms) and magnetic moment are calculated and listed in Table-2. The coeresivity for Ca $Fe_{12-x}Co_xO_{19}$ which linearly decreases with decreasing Co^{+3} ions doped. The continuous decreases of coerecivity, Retentivity, saturation magnetization and magnetic moment with dcreasing Co contents, may be explained by assuming that Co^{3+} substitution is preferentially performed on the spin up magnetic sublattices for the composition. It is evident from the fact that Co ions is magnetic in nature. In these compounds the magnetic moment from octahedraly surrounded ferric ions in the spinal blocks and those in the trigonal bipyramidal sites are opposed by a minority of ferric ions in tetrahedral sites of the spinel block along with octahedral sites. Magnetic hysteresis B-H curve of Cobalt doped calcium hexaferritesas shown in Figure 3. Hysteresis increases with the substitution and maximum for Ca $Fe_{12-x}Co_xO_{19}$. This may be due to the site preference of Cobalt. Calculated values are shown in Table 2. From the squareness ratio it is confirmed that the samples are multi domain.

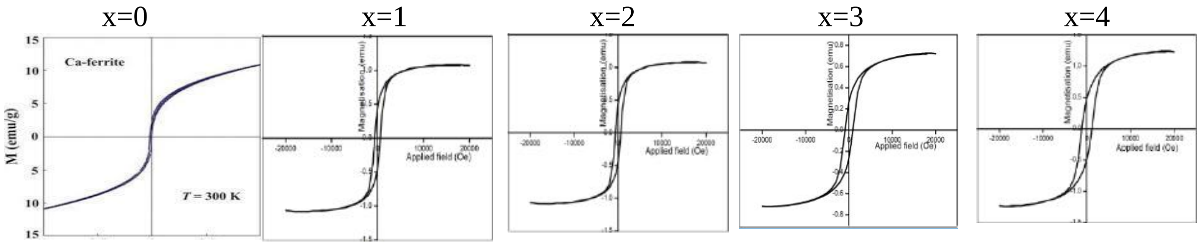


Figure 3: Hysteresis curve of Ca $Fe_{12-x}Co_xO_{19}$ (x=0,1,2,3,4)

Table 2: Magnetic parameters of Ca $Fe_{12-x}Co_xO_{19}$

compounds	Ms (emu/g)	Mr (emu/g)	Hc (Oe)	Mr/MS
$CaFe_{12}O_{19}$	14.6	0.52	489.65	0.356
$CaFe_{11}$ Co O_{19}	26.3	0.95	732.51	0.363
$CaFe_{10}Co_2O_{19}$	45.2	1.66	874.52	0.367
$CaFe_9$ Co_3 O_{19}	62.8	2.47	1141.27	0.394
$CaFe_8$ Co_4 O_{19}	64.6	2.68	634.14	0.415

4. CONCLUSIONS:

In this investigated series of cobalt substituted calcium hexaferrite samples with chemical formula Ca $Fe_{12-x}Co_xO_{19}$ (x = 0, 1, 2, 3, 4) have been prepared using solution auto combustion technique. The X-ray diffraction patterns reveal the formation of hexagonal structure with space group P63/mmc, without any trace of secondary phases. A decrease in the lattice parameter ‘c’ with increasing Co^{3+} substitution is due difference in ionic radii of Co^{3+} ion (0.61 Å) and Fe^{3+} ion (0.65 Å). Increasing the amount of Cobalt affected the morphology of the particles. Agglomeration is increased with the increase of cobalt content. From SEM it is confirmed that the particles are Nano particles. The electrical conductivity of Ca $Fe_{12-x}Co_xO_{19}$ at different concentrations substitution has been explained on the basis of the hopping mechanism of holes (Co^{2+} and Co^{3+})& electrons (Fe^{2+} and Fe^{3+}). As evident from the change in slope of the Arrhenius plot at temperature, the variation in the dc electrical conductivity of pure Ca $Fe_{12-x}Co_xO_{19}$ (x = 0) and substituted Co^{3+} ions in calcium ferrite Ca $Fe_{12-x}Co_xO_{19}$ (x =1, 2, 3, 4) shows a definite kink, which corresponds to ferromagnetic to paramagnetic transitions. The activation energy in the paramagnetic region is higher than the ferromagnetic region. Ferrite with the presence of Co leads to a decrease in activation energy and a decrease in conductivity because there is a significant decrease in crystallite shape area. The presence of Co in ferrites leads to disorder and hence to localization of electrons, leading to the metal–insulator transition-like properties of the Anderson model. The lattice disorder plays a significant role in determining dc conductivity behavior of such ferrites. It was found that replacement of Fe^{+3} with concentration of Co^{+3} leads to an increase in saturation magnetization, remanent magnetization and a significant increase in the coercive field. From the values of Squareness ratio it is clear that the particles are multi domain.

5. ACKNOWLEDGEMENTL

Author is thankful to UGC New Delhi, INDIA for providing financial assistance to carry out this work under minor research project scheme File No 47-1345/10(WRO). Author also thankful to D.K.Kulkarni, J.M.Khobragade, K.G.Rewatkar and S.B.Khasare to guided me for these synthesis and characterization and their analysis of cobalt substituted calcium ferrites.

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