Structural and Electrical Properties of Chromium substituted Nano Calcium

Ch. Mamatha, G. Sankara Rao, V. Krishna Murthy and M. Krishnaiah

Abstract--Nano technology is attracting researchers due to the great applications. Synthesis of one-dimensional nanostructure materials are one of the most exciting area in materials science due to their unique physical property and their potential applications in Nano scale devices and has received considerable attention during the past several years. Chromium substituted M-type Hexaferrites are ferrimagnetic materials in nature. Series of Chromium substituted Calcium Hexaferrite samples with composition CaFe12-xCrxO19 (0 ≤ x ≤ 4), have been prepared by Solution combustion synthesis. The structural properties and morphology of the samples were studied with XRD, and SEM. Electrical properties were carried out with the help of LCR meter. The XRD data of all samples have confirmed the formation of single-phase M-type hexagonal ferrites with the space group of P63/mmc. Grain size, lattice parameters a, c and volume of the samples are calculated. Volume of the cell is found to decrease with increase in the Chromium content. The SEM analysis revealed that the particles are of uniform grain morphology and Nano in size. Frequency dependency and temperature dependency of Electrical properties are studied and Resistivity at room temperature, Activation energy and transition temperature are reported.

Keywords: Nano Ferrites, Combustion, Activation energy, Transition temperature.

I. INTRODUCTION

Calcium Hexaferrites are ferrimagnetic materials, which are also called as M-type hexaferrites since they belong to the family of magneto plumbite. M-type hexaferrites are the most popular due to their large applications as permanent magnets. Substituted Calciumhexaferrites with general formula $CaM_xFe_{12-x}O_{19}$ where M is trivalent ion, are of the significant attractions for researchers because of their enhanced properties and applications in the field of material science as permanent magnets, microwave devices, magnetic storage devices [1], [2], [3], [4], [5].

The magnetic nature of magnetoplumbites is determined by the substituted trivalent ions for ferric ions that occupy different sites in the structure[6], [7], [8], [9], [10].The Fe^{+3} ions when replaced partially by other trivalent metal ions, properties of the calcium ferrites would get altered[11], [12].

To prepare Hexagonal ferrites, various synthesis methods like chemical co-precipitation [13], hydrothermal[14], sol-gel[15], [16] combustion[17] etc. have been developed. In the present work, Calcium hexaferritessubstituted with trivalent Cr^{+3} ions, synthesized by combustion method are studied and reported.

II. EXPERIMENTAL

a. Synthesis techniques

Calcium hexaferrites substituted with trivalent Cr ions with general formula $CaCr_xFe_{12-x}O_{19}$ (0 ≤ x ≤ 4) have been synthesized successfully by solution combustion technique. Samples were prepared with AR grade calcium nitrate, iron nitrate and Chromium nitrate. ODH (C2H6N4O2) was used as fuel. Samples were calcinated at 900°C for 3 hours and allowed to cool gradually [18],[19].

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b.   Structural studies

The structural characterization of the samples was performed by PANalyticalX'pert Pro diffractometer with Cu-Ka radiation (λ=1.5405Å) in the 2θ range of 10-80, in angular steps of 0.02°. The average particle size, D, was determined from line broadening of (107) reflection using Scherrer formula given by

$$D = \frac{K\lambda}{\beta\,Cos\theta}$$

(**1**)

Where β is the angular line width at half maximum intensity and θ the Bragg angle of the height peak. Values of lattice constant 'a' and 'c', unit cell volume 'Vcell', bulk density ρm, X-ray density ρx-ray and Porosity 'P' were calculated by using following equations.

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

(2)

$$V_{cell} = 0.866\,a^2\,c$$

(3)

$$\rho_m = \frac{m}{\pi r^2 h}$$

(4)

$$\rho_{x-ray} = \frac{2M}{N_A V_{cell}}$$

(5)

$$P = 1 - \frac{\rho_m}{\rho_{x-ray}}$$

(6)

Where β is the angular line width at half maximum intensity and θ the Bragg angle of the height peak. Values of lattice constant 'a' and 'c', unit cell volume 'Vcell', bulk density ρm, X-ray density ρx-ray and Porosity 'P' were calculated by using following equations and compared.

c.   Electrical and dielectric studies

Dielectric measurements were carried out at room temperature using LCR meter over a wide frequency range from 100 Hz up to 1 MHz. The dielectric constant (ε') and dielectric loss (tan δ) were calculated using the following formulae.

$$\varepsilon' = \frac{cd}{\varepsilon_0 A}$$

(7)

$$\varepsilon'' = \varepsilon' tan\delta$$

(8)

Where 'c' is the capacitance, 'd' is thickness of the sample, 'A' is the area of cross section and 'ε0'is permittivity of free space.

The AC conductivity measurements were recorded out in the range of frequencies 100Hz-1MHz. at room temperature and DC measurements were recorded in the range of temperatures 310k – 650K. Activation energies are calculated tabulated.

The relation between electrical conductivity and temperature is given by

$$\sigma = \sigma_0 \exp(-E_a/KT) \qquad (9)$$

Where, T is absolute temperature, k is Boltzmann's constant and Ea is the activation energy that is the energy needed to release an electron from the ion for a jump to neighboring ion, giving rise to the electrical conductivity.

III.   RESULTS AND DISCUSSION

a.   Structural analysis

X-ray diffraction spectrum for all the samples is shown in Fig. 1. X-ray diffraction studies confirm the formation of hexaferrites with the space group P63/mmc. The major intensity diffraction peaks of samples have been found at (006), (107), (202), (109), (214), (303), (222) and (224) orientations as mentioned in the figure 1.There is a small shift in the peak position with the increase of substituting ion. The volume of the cell also decreases with increasing substitution ion. This is due to the small ionic radius of Cr^{+3} (0.62 Å) compared to the ionic radius of Fe^{+3} (0.65 Å). Structural parameters of the samples are given in table 1 and 2. There is a variation in the particle size with different substitution. The lattice parameters ratio c/a lies inthe range from 3.575 to 3.755 and exhibited the formationof M-type hexagonal structure [20].
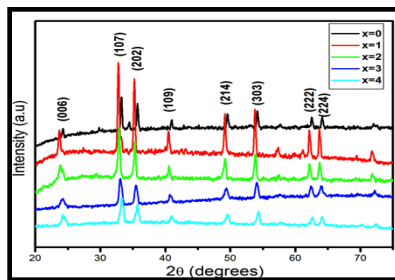

Fig. 1: XRD spectrum of CaCrxFe12-xO19

Fig. 2 shows SEM images of the samples. From the figure it is evident that particles are in Nano size and almost cylindrical in shape. Agglomeration increases with the increase of substitution.
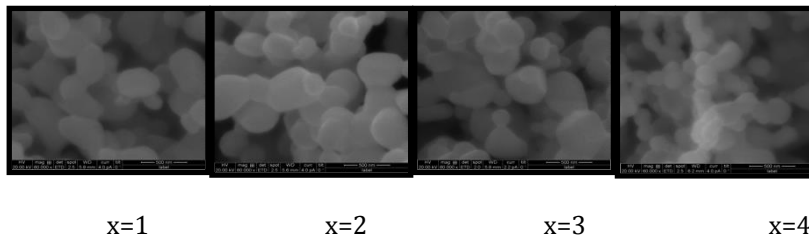
x=1   x=2   x=3   x=4

Fig.2: SEM Images of CaCrxFe12-xO19 (x=1,2,3,4)

Table 1.Structural parameters of CaCrxFe12-xO19.

Sample	D (nm)	'a' (Å)	'c' (Å)	V(Å3)
CaCr1Fe11O19	24	5.986	22.481	698.192
CaCr2Fe10O19	21	5.993	22.379	696.715
CaCr3Fe9O19	16	6.008	22.214	694.963
CaCr4Fe8O19	15	6.018	21.944	688.836

Table 2.Structural parameters of CaCrxFe12-xO19.

Sample	ρm(g/cm3)	ρx-ray (g/cm)	P %	c/a
CaCr1Fe11O19	2.879	4.805	40.08	3.756
CaCr2Fe10O19	3.551	4.797	25.98	3.734
CaCr3Fe9O19	2.908	4.791	39.30	3.697
CaCr4Fe8O19	3.701	4.714	23.14	3.646

b. Electrical and dielectric properties

The variation of dielectric constant and dielectric loss (tan δ) as a function of frequency are shown in Figures (3a and 3b). The value of dielectric constant (ε') and impedance values decreases with increasing frequency up

to 105 Hz. Values are almost constant at higher frequencies. The impedance values rapidly decrease for CaCr4Fe8O19with increasing frequency. Fig. 4a and 4b show the variation of dielectric loss and resistivity with frequency. Resistivity also decreases with increase in frequency.
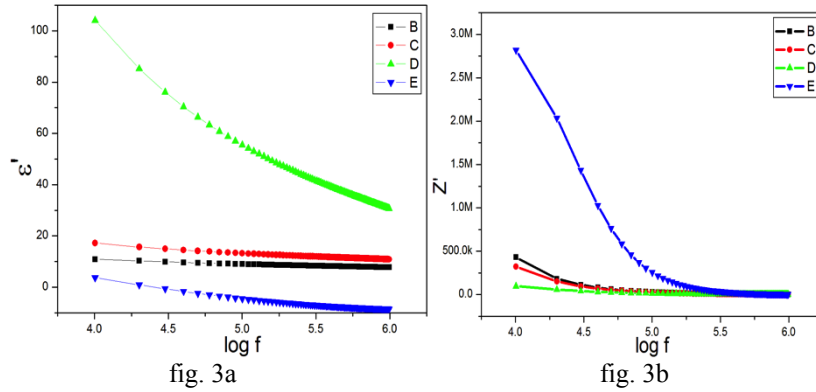

fig. 3a   fig. 3b

Fig. 3: Variation of (a) Dielectric constant and (b) Impedance of CaCrxFe12-xO19 (B,C,D,E for x=1,2,3,4) with frequency.
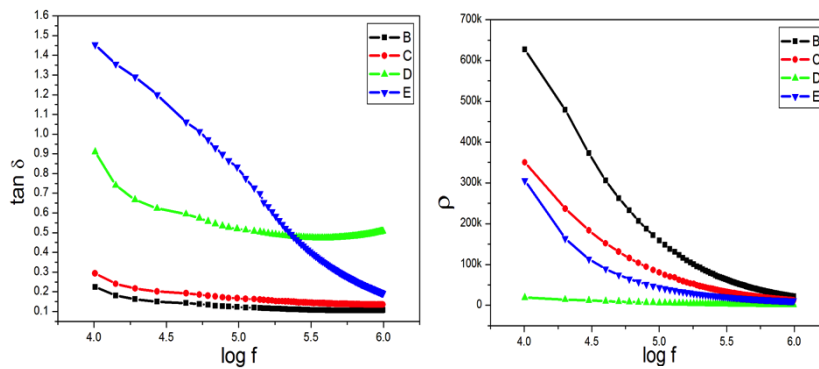

Fig. 4: Variation of (a) Dielectric lossand (b) resistivity of CaCrxFe12-xO19 (B,C,D,E for x=1,2,3,4) with frequency.

From the DC conductivity studies, resistivity at room temperature, activation energy and Transition temperature are calculated and tabulated in table 3. Transition temperature values are found to increase with Chromium substitution.

Table 3.Structural parameters of $CaCr_xFe_{12-x}O_{19}$.

Sample	Resistivity ($\rho M\Omega m$)	Activation energy (eV)	Transition Temperature (K)
$CaCr_1Fe_{11}O_{19}$	2.07	0.59	415
$CaCr_2Fe_{10}O_{19}$	1.46	0.44	476
$CaCr_3Fe_9O_{19}$	3,29	2.4	505
$CaCr_4Fe_8O_{19}$	4.32	0.79	528

IV.   CONCLUSION

A series of Chromium substituted Calcium hexaferrites were prepared using auto combustion technique. The X-ray diffraction patterns reveal the formation of hexagonal structure withspace group P63/mmc for all compounds of Cr3+ substitutions withoutany trace of secondary phases. A decrease in the lattice parameters withincreasing trivalent substitution is due difference in ionic radii of Cr3+ion.Increasing the amount of substitution affected the morphology of the particles agglomeration is increased with increase of substitution.From SEM it is confirmed that the particles are Nano particles. Electrical and dielectric properties are studied and reported.

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