



Effect of cobalt substitution on electrical properties of calcium hexaferrite nano particles

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ABSTRACT

Ferrites are a large class of oxides with remarkable magnetic properties. Their applications include an impressive range extending from millimeter wave integrated circuitry to power handling, simple permanent magnets, and magnetic recording. These applications are established upon the very basic properties of ferrites such as saturation magnetization, high electrical resistivity, low electrical losses, and a very good chemical stability. In the present study a series of Cobalt substituted Calcium Hexaferrite samples with composition $\text{CaFe}_{12-x}\text{Co}_x\text{O}_{19}$ ($0 \leq x \leq 4$), have been prepared by Solution combustion synthesis. The structural properties and morphology of the samples were studied with XRD, and SEM. Electrical properties were studied with the help of LCR meter. The XRD studies of all samples confirmed the formation of single-phase M-type hexagonal ferrites with the space group of $P6_3/\text{mmc}$. Grain size, lattice parameters and volume of the samples are calculated. Volume of the cell is found to decrease with increase in the Cobalt substitution. The SEM analysis revealed that the particles are of uniform grain morphology and Nano in size. Frequency dependency of dielectric properties, frequency and temperature dependency of Electrical properties are studied. Resistivity at room temperature, Activation energy and transition temperature are reported.

Key words: HexaFerrites, Combustion, Activation energy, Transition temperature.

INTRODUCTION

Several researchers with various possible substitutions have extensively studied the properties of M-type hexagonal ferrites by other ions [1-4]. 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. M-type ferrites are considered the basis of the current ceramic permanent magnet industry [5, 6]. They have a prominent position in the permanent magnet market due to their unique combination of acceptable magnetic performance, low cost and chemical stability [7, 8]. The substitutions have had been given in order to improve specific properties of materials, and in the case of the M-type hexaferrites, it has been determined that the substitution can modify their electrical, magnetic, and crystallography properties [10-12]. Substituted Calcium hexaferrites with general formula $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$ 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 [13-17].

The properties of magnetoplumbites are determined by the substituted trivalent ions for ferric ions that occupy different sites in the structure [18-22]. The Fe^{+3} ions when replaced partially by other trivalent metal ions; properties of the calcium ferrites would get altered [23-24].

Different methods are developed to prepare Hexagonal ferrites, such as chemical co-precipitation [25], hydrothermal [26], sol-gel [27], [28] combustion [29] etc. have been developed. In the present work, Calcium hexaferrite substituted with trivalent Co^{+3} ions, synthesized by combustion method are studied and reported.

MATERIALS AND METHODS

2.1 Synthesis techniques

Calcium hexaferrites substituted with trivalent Co ions with general formula $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$ ($0 \leq x \leq 4$) have been synthesized successfully by solution combustion technique. Samples were prepared with AR grade calcium nitrate, iron nitrate, Cobalt nitrate and ODH ($\text{C}_2\text{H}_6\text{N}_4\text{O}_2$) is used as fuel. Samples were calcinated at 900°C for 3 hours and allowed to cool gradually [30],[31].

2.2 Structural studies

The structural characterization of the samples was performed by PANalytical X'pert Pro diffractometer with Cu-K α radiation ($\lambda=1.5405\text{\AA}$) in the 2θ range of 10° - 80° , in angular steps of 0.02° . The average particle size, D , was determined from the highest peak of (107) reflection using Scherrer formula given by

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

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', Volume of the unit cell ' V_{cell} ', bulk density ρ_m , X-ray density $\rho_{\text{x-ray}}$ and Porosity 'P' were calculated by using following equations.

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

$$V_{\text{cell}} = 0.866 a^2 c \quad (3)$$

$$\rho_m = \frac{m}{\pi r^2 h} \quad (4)$$

$$\rho_{\text{x-ray}} = \frac{2M}{N_A V_{\text{cell}}} \quad (5)$$

$$P = 1 - \frac{\rho_m}{\rho_{\text{x-ray}}} \quad (6)$$

Where β is Full width at half maximum and θ is the Bragg angle of the height peak. Values of lattice constant 'a' and 'c', unit cell volume ' V_{cell} ', bulk density ρ_m , X-ray density $\rho_{\text{x-ray}}$ and Porosity 'P' were calculated by using following equations.

2.2 Electrical and dielectric studies

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

$$\epsilon' = \frac{cd}{\epsilon_0 A} \quad (7)$$

$$\epsilon'' = \epsilon' \tan \delta \quad (8)$$

Where 'c' is the capacitance, 'd' is thickness of the sample, 'A' is the crosssectional area and ' ϵ_0 ' is permittivity of free space.

The 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 the following equation.

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

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

RESULTS AND DISCUSSION

3.1 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 $P6_3/mmc$. The major intensity 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 Cobalt substitution. 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 and 2. The lattice parameters ratio c/a lies in the range from 3.574 to 3.66 and exhibited the formation of M-type hexagonal structure [32].

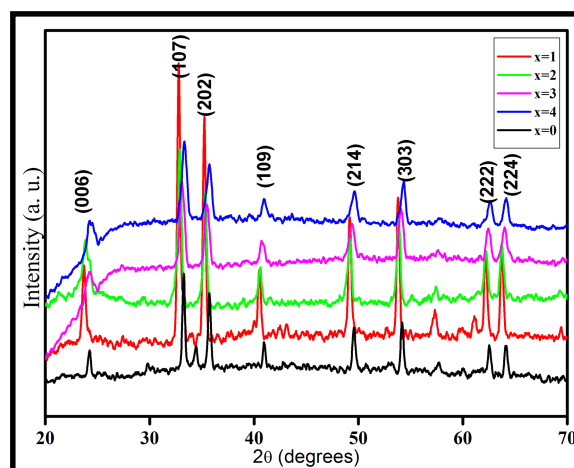


Fig. 1: XRD spectrum of $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$

Fig. 2 shows SEM images of the samples. From the figure it is evident that particles are of uniform grain size and almost cylindrical in shape. Agglomeration increases with the increase of substitution.

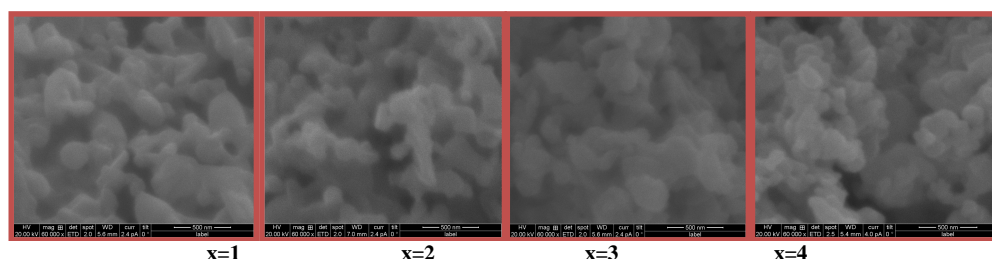


Fig.2: SEM Images of $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$ ($x=1,2,3,4$)

Table 1: Structural parameters of $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$.

Sample	D (nm)	'a' (Å)	'c' (Å)	V (Å ³)
$\text{CaCoFe}_{11}\text{O}_{19}$	27	6.035	22.096	697.686
$\text{CaCo}_2\text{Fe}_{10}\text{O}_{19}$	13	6.044	21.979	695.931
$\text{CaCo}_3\text{Fe}_9\text{O}_{19}$	17	6.055	21.723	690.378
$\text{CaCo}_4\text{Fe}_8\text{O}_{19}$	24	6.050	21.628	686.237

Table 2: Structural parameters of $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$.

Sample	$\rho_m(\text{g/cm}^3)$	$\rho_{x\text{-ray}}(\text{g/cm}^3)$	P %	c/a
$\text{CaCoFe}_{10}\text{O}_{19}$	2.999	4.841	38.05	3.660
$\text{CaCo}_2\text{Fe}_{10}\text{O}_{19}$	2.341	4.868	51.92	3.636
$\text{CaCo}_3\text{Fe}_9\text{O}_{19}$	3.246	4.922	34.06	3.587
$\text{CaCo}_4\text{Fe}_8\text{O}_{19}$	2.922	4.967	41.17	3.574

3.2 Electrical and dielectric properties

The variation of dielectric constant and dielectric loss ($\tan \delta$) 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 10^5 Hz.

The impedance values rapidly with increase in frequency. Fig. 4a and 4b show the variation of dielectric loss and resistivity with frequency. Resistivity also decreases with increase in frequency. Resistivity is almost constant and same for all the samples at high frequencies. The dielectric loss is maximum when three iron ions are replaced with Cobalt ions.

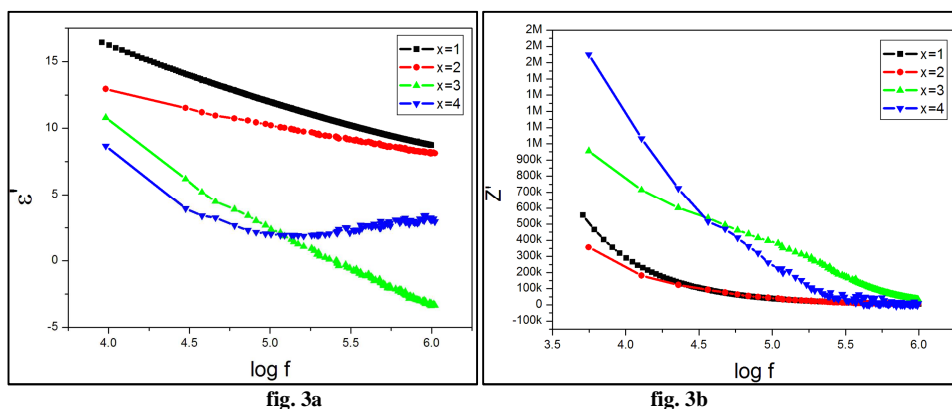


Fig.3: Variation of Dielectric constant and Impedance of $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$ with frequency

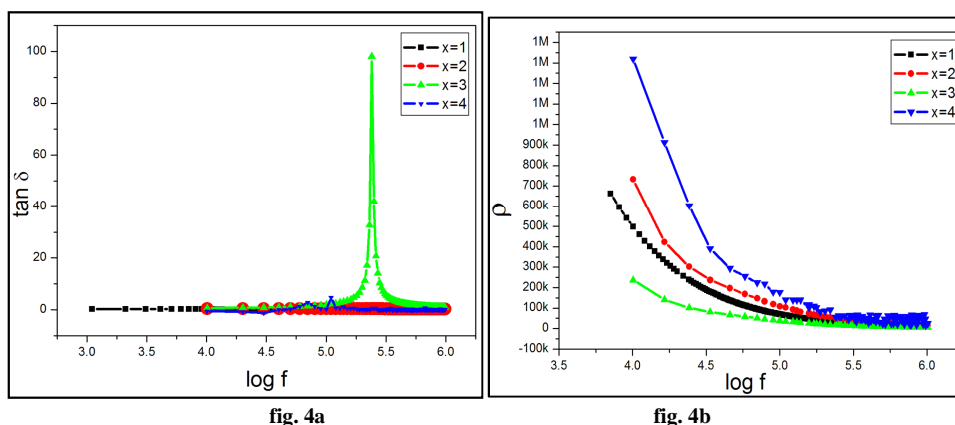


Fig. 4: Variation of Dielectric loss and resistivity of $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$ with frequency.

From the DC conductivity studies, resistivity at room temperature, activation energy and Transition temperature are calculated and tabulated in table 3.

Table 3. Electrical properties of $\text{CaCo}_x\text{Fe}_{12-x}\text{O}_{19}$.

Compound	Resistivity at Room Temp. ρ M Ω m	Activation energy (eV)	Transition Temperature (K)
$\text{CaCo}_{11}\text{Fe}_1\text{O}_{19}$	2.53	0.58	561
$\text{CaCo}_2\text{Fe}_{10}\text{O}_{19}$	3.84	0.59	610
$\text{CaCo}_3\text{Fe}_9\text{O}_{19}$	2.16	0.74	580
$\text{CaCo}_4\text{Fe}_8\text{O}_{19}$	3.31	1.08	621

CONCLUSION

A series of Cobalt substituted Calcium hexaferrites were prepared using auto combustion technique. The X-ray diffraction patterns reveal the formation of hexagonal structure with space group $P6_3/mmc$ for all compounds of Co^{3+} substitutions without any trace of secondary phases. A decrease in the lattice parameters with increasing trivalent substitution is due to the difference in ionic radii of Co^{3+} ions. Increasing the amount of substitution affected the morphology of the particles. From SEM it is confirmed that the particles are Nano particles. Electrical and dielectric properties are studied and reported.

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