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Synthesis and Characterization of Nano-Hexagonal Calcium Ferrites

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ABSTRACT

The comparative study of substituted calcium hexaferrites samples with chemical composition $\text{CaCr}_x\text{Fe}_{12-x}\text{O}_{19}$ where, $x = 0, 2, 4, 6$ have been chosen for their studies on structural and magnetic properties. Structural and morphological properties are studied by X-ray diffraction technique and scanning electron microscopy (SEM). The XRD pattern confirmed that the formation of single phase hexagonal ferrites with space group $P6_3/mmc$ 167:R-3c. The SEM results confirms that the sample exhibit relatively well defined hexagonal like grains with average particle size found in between 24 to 40 nm. Magnetic characterization of the samples is carried out using vibrating sample magnetometer (VSM). The saturation magnetization (M_s), remanence (M_r) and coercivity (H_c) are found to decrease with increase in the value of substitution which is attributed to the occupation of sub lattice spin-up and spin-down sites by diamagnetic ions and anisotropy. The samples have a better signal-to-noise ratio, as the particle size was less than 50 nm, when calculated by Debye-Scherrer formula and may be suitable for recording media.

1. Introduction

Ferrites are broad family of oxides with incredible electrical and magnetic properties. Nano sized ferrite materials have received vital attention because of their wide range of applications in magnetic storage devices [1-3]. The novel magnetic, electric and dielectric properties possessed by them have made ferrites more attractive to the field of science and technology. These important properties of ferrites are popularly used in micro-electric devices, magnetic switches, sensors, microwave devices, electromagnetic circuits, transformer core, and antenna rods in the field of medicines [4-5]. Magnetic properties of ferrites are mainly depends on chemical composition, method of synthesis, temperature conditions, grain size and surface morphology [6-9]. Ferrite properties are possible to alter with synthesis methods, suitable dopant and annealing temperature [10-13]. The wide variety of applications of ferrites as permanent magnets are not only due to their very basic properties, but also because of significant saturation magnetization, high electrical resistivity, low electrical losses, good chemical stability and low cost.

2. Experimental Methods

The fortuity of preparing ferrites in the form of nanoparticles has opened a novel and exciting trend in the research field. There are many methods for synthesis of hexagonal ferrite nanoparticles, like chemical co-precipitation [14], hydrothermal [15], sol-gel [16, 17], combustion [18] etc. In the present work, calcium hexaferrites substituted with trivalent chromium ions synthesized by sol-gel microwave auto combustion method are studied and reported.

Samples were prepared with AR grade calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as raw materials. Chromium nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as substituting material. Urea $\text{NH}_2\text{-Co-NH}_2$ was used as fuel. A series of chromium substituted calcium hexaferrite samples with general formula $\text{CaCr}_x\text{Fe}_{12-x}\text{O}_{19}$, where $x = 0, 2, 4, 6$ have been synthesized by sol gel microwave auto combustion method the solution undergoes dehydration followed by decomposition. In few minutes and upon reaching spontaneous combustion, the solution ignites like smoldering with evolution of a large volume of gases. It releases large amount of heat vaporizing all the solution to become a solid at 430 °C.

Prepared powders are loose, foamy, pores and highly friable. The samples crushed into powder using agate motor were sintered at 900 °C for four hours and allowed to cool gradually on sand bath [19-21].

3. Result and Discussion

The structural characterization of substituted nano-hexa ferrites was done by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

3.1 X-Ray Diffraction Analysis

The particle size of the powder samples was calculated by the Debye Scherrer equation, $D = K\lambda/\beta\cos\theta$, where k is Scherer constant ($k = 0.89$, for hexa - ferrites), λ is wavelength of X- rays 1.5405 Å, β is Full Width of Half Maxima (FWHM) and θ is the Bragg's angle [10]. The estimated average particle size is found in between 24 to 30 nm. The value of lattice constant a , c and the unit cell volume (V_{cell}) were calculated by taking $(h k l)$ parameter and inter planar distance (d), X-ray density ($\rho_{\text{x-ray}}$) and porosity were calculated by using following equations [11].

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

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

$$P = 1 - \frac{\rho_m}{\rho_{\text{x-ray}}} \quad (3)$$

$$\rho_{\text{x-ray}} = \frac{ZM}{V N_A} \quad (4)$$

where, M is the molar mass, V is cell volume, N_A is Avogadro's number. Structural parameters are recorded in the Table 1 and Fig. 1.

Table 1 Structural parameters of $\text{CaCr}_x\text{Fe}_{12-x}\text{O}_{19}$ where $x = 0, 2, 4$ and 6

Conc. (x)	D (nm)	a (Å)	c (Å)	V (Å ³)	Bulk density (g/cm ³)	Porosity	c/a	X ray density (g/cm ³)
0	24	5.892	21.325	699.489	2.852	40.753	3.619	5.255
2	30	5.993	22.379	696.715	3.551	25.982	3.734	4.797
4	25	6.018	21.944	688.237	3.701	23.136	3.646	4.815
6	28	6.043	21.509	680.210	3.975	21.567	3.559	4.135

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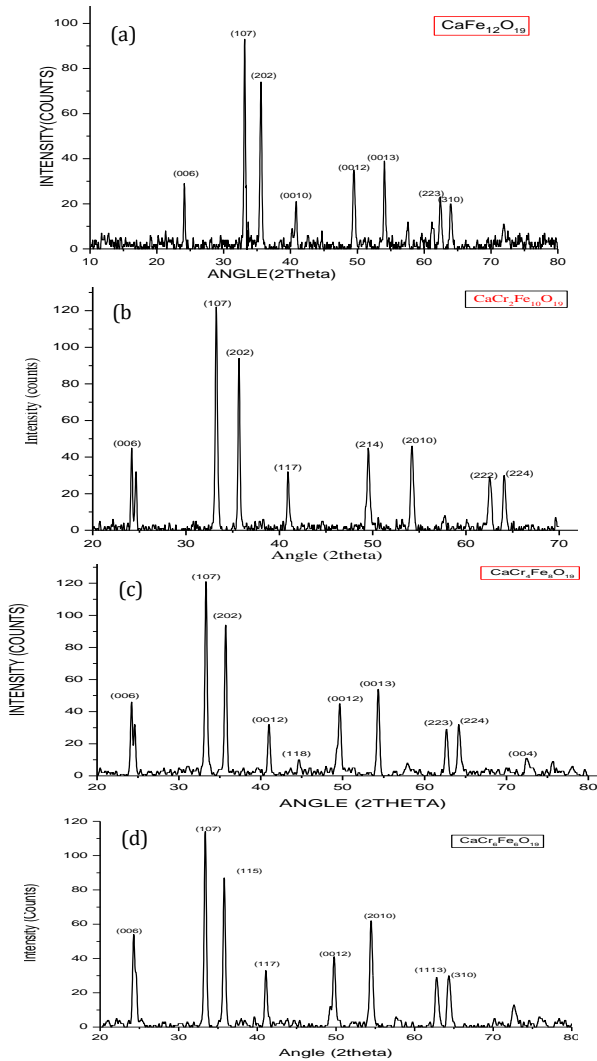


Fig. 1 XRD spectrum of (a) $\text{CaFe}_{12}\text{O}_{19}$, (b) $\text{CaCr}_2\text{Fe}_{10}\text{O}_{19}$, (c) $\text{CaCr}_4\text{Fe}_8\text{O}_{19}$ and (d) $\text{CaCr}_6\text{Fe}_6\text{O}_{19}$

3.2 Micro Structural Analysis

The SEM images of the samples are shown in Fig. 2. It is evidence that the particles are in nano size and almost hexagonal in shape.

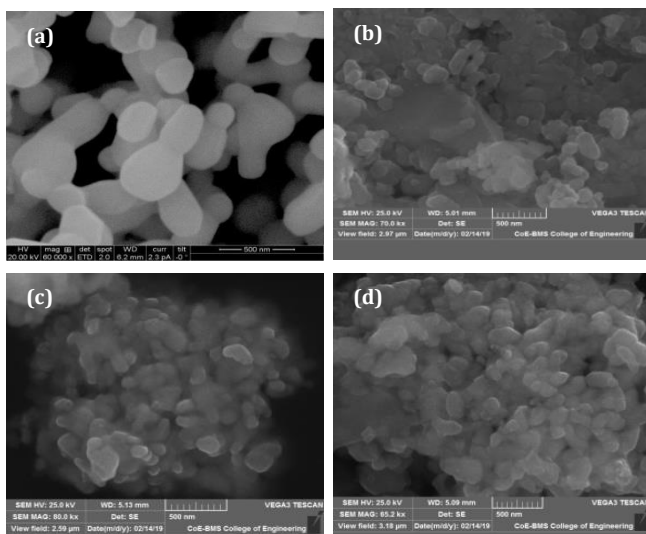


Fig. 2 SEM images of (a) $\text{CaFe}_{12}\text{O}_{19}$, (b) $\text{CaCr}_2\text{Fe}_{10}\text{O}_{19}$, (c) $\text{CaCr}_4\text{Fe}_8\text{O}_{19}$ and (d) $\text{CaCr}_6\text{Fe}_6\text{O}_{19}$

3.3 Magnetic Studies

Hysteresis curves for the samples shows magnetic behavior of the sample in the presence of external magnetic field are shown in the Fig. 3. The saturation magnetization (M_s), remanence (M_r) and coercivity (H_c) found to decrease with increase in the value of substitution mentioned in Table 2 which is attributed to the occupation of sub lattice spin-up and <https://doi.org/10.30799/jnst.302.20060204>

spin-down sites by diamagnetic ions and anisotropy [19]. This result indicates that the saturation magnetizations of the chromium substituted calcium ferrites are lower than those of the undoped sample. This is certainly due to the diffusion of Cr into calcium hexaferrite structure. There are two factors to explain the change in magnetization. One of them is the distribution of Cr^{3+} ions on the five crystallographic sites of the calcium ferrites. The Cr^{3+} ions entering spin up sub lattices would lead to the small decrease in the saturation magnetization while on the other hand if they enter spin down sub lattices would result in the small increase in the saturation magnetization. However, the saturation magnetization decreases with increasing Chromium content. This may be concluded that Cr^{3+} ions occupy only spin up 12k, 2a, and 4e sites. The ion occupies octahedral site when the ratio of radius of positive ion to that of negative ion is in between 0.414 – 0.73.

The ratio of Cr^{3+} (0.62) and O^{2-} (1.4) is 0.436. Another reason is a magnetic dilution, which are due to the substitution of the Fe^{3+} ions (5 μB) by Cr^{3+} ions (3 μB). It is, therefore, understood that the Fe^{3+} - O - Fe^{3+} super exchange interaction decreases with increasing Cr diffusion. This indicates that the saturation magnetization decrease with the Cr doping content. From the magnetization curve the squariness (SQR) ratio is determined found to be less than 0.5. This means for all samples are multi domain. Calculated magnetic parameters such as saturation magnetization, remanent magnetization and coercivity are given in Table 2. Coercivity is found to be more for $\text{CaCr}_2\text{Fe}_{10}\text{O}_{19}$. The decrease in the value of coercivity, H_c with increase in the value of x can be attributed to lowering of magneto crystalline anisotropy according to M.V. Cabanas et al. [20,21].

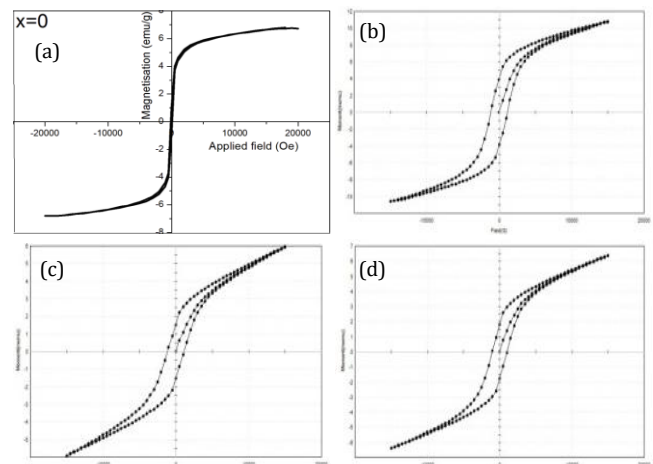


Fig. 3 Hysteresis curves for (a) $\text{CaFe}_{12}\text{O}_{19}$, (b) $\text{CaCr}_2\text{Fe}_{10}\text{O}_{19}$, (c) $\text{CaCr}_4\text{Fe}_8\text{O}_{19}$ and (d) $\text{CaCr}_6\text{Fe}_6\text{O}_{19}$

Table 2 Magnetic properties of $\text{CaCr}_x\text{Fe}_{12-x}\text{O}_{19}$ where x= 0, 2, 4, 6 (a,b,c,d)

Conc. (x)	M_s (emu/g)	M_r (emu/g)	M_r/M_s	H_c (Oe) G	$K(J/m^3)$	BM (μB)
0	20.268	2.9320	0.144	217.09	4.5833	3.6800
2	10.717	3.8645	0.360	1174.5	12.586	1.9313
4	6.3855	1.7918	0.280	1026.6	6.5553	1.1419
6	5.9392	1.5241	0.256	1148.9	6.8235	1.0539

4. Conclusion

The X-ray diffraction analysis of all samples confirms the formation of single phase M-type hexagonal structure. The average size of the particles deduced from XRD peak broadening have been observed in the diameter of the particle is 24 nm and 40 nm. The values of the lattice parameters, morphological structural study support conforms, the synthesized samples are found to be with space group 167:R-3c, hexagonal of $P6_3/mmc$. VSM analysis confirms the saturation magnetization (M_s), remanence (M_r) and coercivity (H_c) are found to be decreased with increase in the value of x substitution which is attributed to the occupation of sub lattice spin-up and spin-down sites by diamagnetic ions and anisotropy.

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