



**MORPHOLOGICAL AND DIELECTRIC BEHAVIOR OF CR
SUBSTITUTED NANOSIZED CALCIUM HEXAFERRITES BY SOL GEL
AUTO COMBUSTION TECHNIQUE.**

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Abstract

The polycrystalline samples of calcium substituted mixed nanoferrites $\text{CaFe}_{12}\text{O}_{19}$, $\text{CaCr}_{0.5}\text{Fe}_{11.5}\text{O}_{19}$ and $\text{CaCr}_1\text{Fe}_{11}\text{O}_{19}$ were prepared by sol gel auto combustion method in which the urea was used as a fuel. The XRD pattern of prepared samples confirms M type hexagonal single phase crystalline structure. Using XRD analysis, lattice parameters, size of atoms have been determined. The morphological investigations and nanometric sizes of the samples were studied by using scanning electron microscopy. The samples were subjected to study the variation of dielectric constant as well as loss tangent with *log* frequency. All samples follows the Maxwell Wranglers' interfacial polarization.

1. Introduction

The ferrites are low cost and high performance electromagnetic materials, which are generally found useful in microwave devices and memory core applications [1]. Depending upon desired applications of ferrites its properties can be modified by substitution of different ions. The characteristic of ferrites depends upon nature and number of substituted ions [2]. Recently the ferrite researches have been shifted towards developing ferrites on nanometric scales as technological advantages in electronics industry demands compact cores for work at higher frequencies [3,4]. The M type hexaferrites are very good dielectric materials and very useful for microwave applications [5]. To prepare nanosized ferrite particles several methods were investigated, some of



them are co-precipitation of hydroxides, sol gel synthesis, hydrothermal synthesis, solid state method, ball milling, etc [6-9]. All methods produce same microstructure but in current research module we used the sol gel auto combustion method to synthesis the calcium substituted hexaferrites powders as this method is simple, safe, rapid and main advantages of this method are high homogeneity, high purity and producing ultrafine powders [6]. The purpose of this research is to investigate the role of Cr substitution on structural and dielectric properties of prepared samples.

2. Experimental

For preparation of samples AR grade compounds of calcium nitrate $[\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$, Iron nitrite $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ and Chromium nitrite $[\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ were used, while the urea was taken as the fuel. The stoichiometric proportion of all the AR grade compounds were dissolved in 100% pure AR grade distilled water. The above solution was continuously stirred and heated at 60°C for about two hours till homogenous viscous gel was formed. This gel was then kept in micro oven and temperature of oven was increased up to 800°C . The auto combustion were started, the gel automatically ignited and burns with glowing flints and gases comes out. The auto combustion process were completed within five minutes, yielding brown coloured powder (ash). The powder obtained was then collected, grinded unidirectionally in pestal mortar for about five hours so that fine powder of nanosized particles were prepared. Then, the palates were prepared by pressing this powder in hydraulic press for twenty minutes at 40 lbs pressure. These palates were then heated in electric furnace up to 500°C for about 5 hours by increasing temperature slowly and then cooled at same rate. The palates thus formed were then broken and finally converted into fine powder of nanosized particles by grinding unidirectionally in pestal mortar for about 5 hours. To study some of the characteristics this powder was



used. In remaining powder few drops of 5% polyvinyl acetate for strong bonding between different atoms were added and again for an hour and palates were prepared. These palates were then kept in furnace and heated slowly up to 400°C for about 2 hours to remove polyvinyl acetate and impurities of different kinds. These plates were then used to study electrical and magnetic characteristics.

3. Characterization

The powder samples of all specimens were then subjected to characterization. X-ray diffraction patterns of the samples were taken on Phillips expert diffractometer using Cu K α radiation ($\lambda=1.540598 \text{ \AA}$) at data angle (2θ) range of 30.0084 to 69.9924 degree, with step size of 0.017° and an accuracy of 0.001° at 45 KV and 40 mA. The lattice parameters, crystalline (grain) size of the prepared samples were calculated from the XRD data. The scanning electron microscope (SEM) and transmission electron microscope (TEM) was used to study morphology and estimate grain size. The loss factor($\tan\delta$) were measured by using Precision Impedance Analyzer (Wyne Kerr 6500B)in the frequency range 100Hz to 1MHz at room temperature and corresponding dielectric constant were also calculated.

4. Result and discussion

4.1: Structural analysis

The figure (1) shows the XRD pattern of the samples. The diffraction peaks shows the formation of ferrite phase in all samples. Absence of secondary phases in XRD pattern gives the evidence of formation of purely crystallized single phase [10] hexagonal M-structure pertaining to space group (SG:p6₃/mmc)(no194) [6].The substitution ratio do not affect the lattice parameters. This investigates that replacement of Fe⁺³ by Cr⁺³ is due to resemblance in their ionic radii.

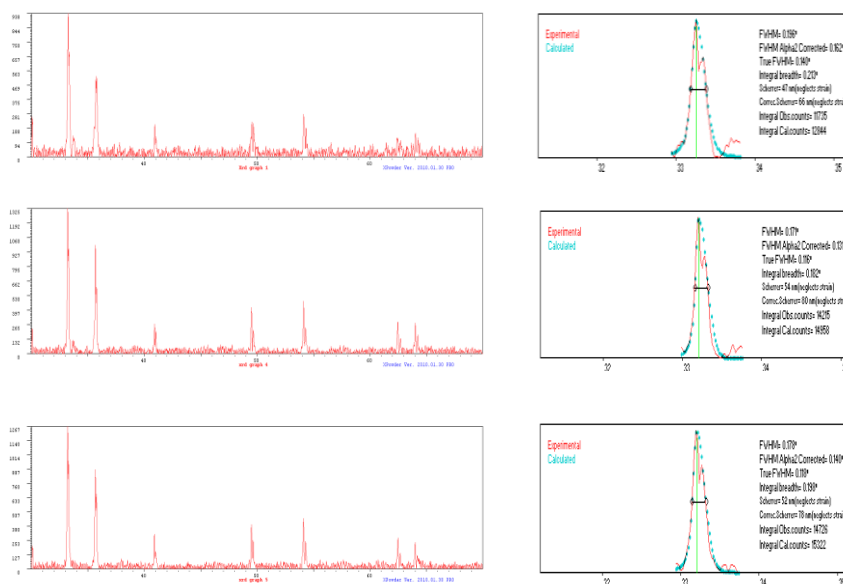
The average particle size (D) for each composition were calculated from the peak of highest intensity by using Scherer's formula

$D = k\lambda/\beta\cos\theta$, where k is Scherer factor (0.9), λ is X-ray wavelength. Here $\lambda=1.540598 \text{ \AA}$, β is line broadening of peak at angle θ (shown in figure 1). The β is measured using the equation

$\beta = (B^2 - b^2)^{1/2}$ where B is FWHM of the experimental profile in degrees and b is the instrumental broadening [4,10]. The calculated lattice parameters, other related data and average size of the ferrite particles for all samples are listed in table 1. It shows that the particle sizes of the ferrite samples were in the range 50 nm, which were confirmed by TEM studies.

Table 1: Structural data

s.no.	sample	Lattice parameters		Cell volume (\AA^3)	Bulk density, $d=\text{gm}/\text{cm}^3$	X-ray density, $dx=\text{gm}/\text{cm}^3$	Porosity %	Particle size D nm
		a(\AA)	c (\AA)					
1	CaFe ₁₂ O ₁₉	5.8210	22.1120	648.81	2.4789	5.1862	0.522	47 nm
2	CaCr _{0.5} Fe _{11.5} O ₁₉	5.8190	22.0440	646.01	3.3033	5.2008	0.3649	54 nm
3	CaCr ₁ Fe ₁₁ O ₁₉	5.8112	22.1120	643.19	3.3529	5.2020	0.3554	52nm



Fig(1):XRD pattern and broadening of respective high intensity peak.

4.2: Scanning Electron Microscopy (SEM):

SEM determines the average grain size and type of grain growth of the samples which influences magnetic properties of the sample. The SEM micrographs of the prepared samples are shown in figure (2). The average grain sizes of the prepared samples are determined from the micrographs. It is found that the average grain sizes of the samples after substitution of Cr^{3+} are nearly remains same this is due to resemblance of ionic radii of Fe^{3+} with Cr^{3+} (64pm)

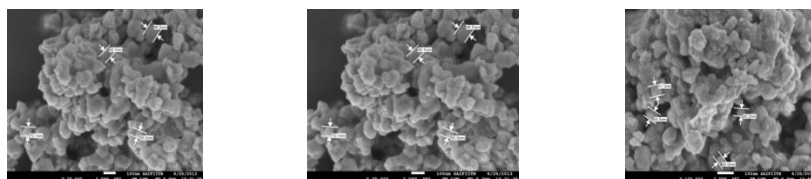


Fig2: SEM micrographs of prepared samples

4.3: Electrical property:

The value of the dielectric constant (ϵ') was calculated by using the formula

$\epsilon' = Ct/\epsilon_0A$, Where C is the capacitance, t the thickness, A the area of cross section of palate and ϵ_0 is constant called permittivity of free space [5]. Figure (3) shows the variation of dielectric constant ϵ' against \log of the frequency (f) for all prepared samples. From graph it is seen that For all compositions dielectric constant ϵ' decreases with increase in frequency. This behavior is just like a normal ferromagnetic behavior. The value of dielectric constant is large at small frequency which decreases rapidly with increase in frequency and becomes constant. The dispersion in dielectric constant is due to Maxwell Wrangler type interfacial polarization which is in good agreement with Koop's phenomenological theory [11,12]. The large value of dielectric constant ϵ' at lower frequency is due to charge accumulation at interfaces, oxygen

vacancies, interfacial distribution, grain boundary defects etc [13]. The process of polarization in ferrite is similar to conduction mechanism. The polarization causes due to electron hopping exchange between ion of same element present in more than one valence state ($\text{Fe}^{3+} + \bar{e} \rightarrow \text{Fe}^{2+}$) [14]. At high frequency of applied field the electron hopping does not follow the alternating field due to this value of dielectric constant ϵ' decreases and finally attains a certain constant value.

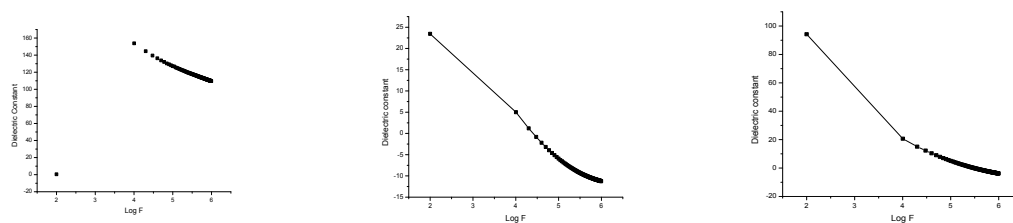


Fig3: variation of dielectric constant (ϵ') against $\log F$ for prepared samples

Figure (4) shows the variation of dielectric loss ($\tan\delta$) against \log frequency for prepared samples. From graph it is found that dielectric loss decreases with increase in frequency. In all samples dielectric loss decreases rapidly in low frequency region (100Hz to 1kHz), then decreases slowly in high frequency region (1kHz to 1MHz) and finally it becomes constant. This behavior is similar to frequency dependent behavior of dielectric constant. The initial rapid decrease in dielectric loss ($\tan\delta$) with increase in frequency can be explained on the basis of Koop's phenomenological model [14].

5: Conclusion:

The sol Gel Auto combustion technique yields nanocrystalline single phase hexagonal crystal structure for all the samples. The average practical size of the composition varies from 47nm to 52nm. The a and c values favors' the formation of hexagonal crystal structure, also the Values obtained from SEM results supports the results. Bulk density increases after doping of Cr^{3+} ions and porosity decreases but X-ray



density remains nearly same. The value of dielectric constant increases with increase in concentration of Cr^{3+} ions. The value of dielectric constant is large at low frequency and decreases with increase in frequencies can be explained on the basis of space charge polarization (Koop's Model). The dielectric constant and dielectric loss factor both shows same nature with increase in frequency.

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