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INFLUENCE OF SUBSTITUTION OF ALUMINIUM ON STRUCTURAL AND DIELECTRIC PROPERTIES OF NANOSIZED M-TYPE CALCIUM FERRITES

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ABSTRACT:
The sol–gel auto-combustion technique was adopted to synthesize single-phase nanosized M-type hexagonal ferrites (NHFs) with the composition of $CaAl_xFe_{12-x}O_{19}$ (x=2, 4 and 6). The structural properties of the synthesized samples were carried out by XRD analysis. The XRD analysis revealed that the samples are a single phase M-type hexagonal ferrite. The lattice parameters, Cell volume, X-ray density and bulk density porosity of samples were found to be decreasing with increase in the substitution of aluminium where as the porosity of the samples increases with increase in the substitution of aluminium. The average particle size of the samples measured by TEM is found to be in the nano-range. The dielectric constants (ε′) of the samples were measured at fixed frequency of 1 MHz with different temperature. The dielectric constant of the samples increases with increase in temperature. The dielectric constant decreases with increase in concentration of Al^{3+} ions in substituted NHFs accompanied by an increase in the electrical resistivity are suitable trends for applications in the microwave devices

Keywords:- M-type hexagonal ferrite, structural property, dielectric constant, sol-gel auto-combustion technique, TEM.

INTRODUCTION :

Ferrites are the ceramic compounds which much high electrical resistivity than the metallic ferromagnetic materials. They can be divided into three categories namely spinel, hexagonal and garnets according to their crystal lattice structure [1]. The ferrites having formula $MFe_{12}O_{19}$ (M = Ca, Ba, Sr, Pb), are those ferrites which have magnetoplumbite structure commonly known as hexagonal structure. The hexagonal ferrites containing calcium as divalent cations are the best ferrites [2].

Dielectric properties of ferrites are dependent upon several factors, including method of preparation, chemical composition and grain size [3, 4]. Since the ferrites are widely used components in microwave family due to their high electrical resistivity, low magnetic and dielectric losses [5, 6], we investigated the dielectric behavior of aluminium substituted calcium hexaferrites at fixed frequency over wide range of temperature. In the present study, we have synthesized $CaAl_xFe_{12-x}O_{19}$ NHFs by sol-gel auto combustion technique. The influence of substitution of Al^{3+} ion for Fe^{3+} ion on structural and dielectric properties of NHFs have also been investigated

Experimental :-

Sample preparations

Sol–gel auto-combustion synthesis method (also called low-temperature self-combustion, auto-ignition or self-propagation, as well as gel-thermal decomposition) where the chemical sol–gel and combustion process is combined

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calledlow-temperature self-combustion, auto-ignition or self-propagation, as well as gel-thermal decomposition) where the chemical sol–gel and combustion process is combined

Sol–gel auto-combustion synthesis technique is also known as low-temperature self-combustion or auto-ignition technique. The unique combination chemical sol–gel and combustion process has shown great potential in the synthesis of M-type nanoferrites .

The aluminium substituted calcium hexaferrite powders have been synthesized by microwave assisted sol-gel auto-combustion technique. The synthesis technique was the unique combination of sol-gel method and combustion method. In this technique, the metal nitrates acted as an oxidizing reactant and urea as a reducing reactant. The initial composition of solution containing metal nitrates and urea was based on the total oxidizing and reducing valences of the oxidizer and the fuel using the concept using the concept of propellant chemistry [7,8]. Carbon, hydrogen and aluminium were considered as reducing elements with the corresponding valences +4, +1 and +3 respectively. Oxygen was considered as an oxidizing element with valence of -2, the valence of nitrogen was considered to be 0. The total calculated valence of calcium nitrate, aluminium nitrate and ferric nitrate by arithmetic summation of oxidizing and reducing valences were -10, -15 and -15 respectively. The calculated valences of urea was +6. The stoichiometric composition of redox mixture demanded that 1(-10)+2(-15)+10(-15)+n(+6)=0 or n=31.667 mol.

The appropriate amounts of AR grade $Ca(NO_3)_2{\cdot}4H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $Al(NO_3)_3.9H_2O$ and fuel urea $CO(NH_2)_2$, dissolved in a minimum quantity of water, were placed in a beaker. The solution in beaker was introduced into a microwave oven. Initially the solution boils and undergoes dehydration followed by decomposition with the evolution of a large volume of gases (N_2 , NH_3, and HNCO) during combustion reaction [9,10]. After the solution reaches the spontaneous combustion, it begins burning and releases lots of heat, vaporizes all the solution instantly and becomes a solid burning at temperatures above 1000 °C. The ashes obtained after combustion were brown and voluminous. The ashes formed were crushed in the agate mortar to fine calcium hexaferrites powder.

The 10% polyvinyl alcohol solution (2–3 drops) had been mixed before they were pressed by hydraulic press into pellets of 15 mm in diameter and about 5–8 mm in thickness using a stainless steel die set under uniaxial appropriate pressure for 5 min. The Poly Vinyl Acetate was used as a binder. The pellets of the sample was calcined at 800 °C for about 2 hours in the electric furnace to obtained monophase M type calcium hexaferrites. Both surfaces of the pellet samples were coated with silver paste for better electrical contact to study its electrical properties. Figure 1 (a) shows peak reaction stage in microwave oven and (b) shows ash obtained after combustion.

Characterization

Philips Holand X-ray diffractometer (PW 1710) was used to determine the crystalline phases of the samples. The Copper Kα-radiation source with a wavelength of 1.54056 Å was used in this characterization.

The lattice parameter 'a' and 'c', the unit cell volume (V), X-ray density (ρ_X), bulk density (ρ_B) and porosity (P) were calculated by using following equations.

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

Where d is the inter planer distance,
h, k, l are Miller indices of the plane,
a and c are the lattice constants

$$V = 0.8666a^2c \quad (2)$$

$$\rho_X = \frac{ZM}{NV} \quad (3)$$

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Where, Z is the number of formula units in a unit cell which is 2 for M type hexaferrite

M is molecular weight, N is Avogadro number, V is the unit cell volume.

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

Where, m is the mass of the circular pellet, r is the radius of the pellet, h is height of the pellet.

$$P = 1 - \frac{\rho_B}{\rho_X} \quad (5)$$

Where, P is porosity, ρ_B is bulk density, ρ_X is X-ray density.

The dielectric constant (έ) of the sample was calculated by the formula

$$\acute{\varepsilon} = C\, d \,/\, \varepsilon_o A \quad (6)$$

where

C is the capacitance of the pellet in Farad

d is the thickness of the pellet in meter

A is the area of cross-section of flat surface of the pellet and

ε_o is permittivity of free space

The particle size of the samples were calculated by Debye–Scherrer equation given as

$$D = \frac{k\lambda}{\omega \cos\theta} \quad (7)$$

Where, k is known as the Scherer's constant and its value is 0.9

λ is the wavelength of X-ray (1.54056 Å)

ω is the full width at half maximum (FWHM) of the diffraction peak in radian

θ is Bragg's angle

RESULTS AND DISCUSSION :-

XRD analysis

Figure 2 reveals that the X-ray diffractograms of $CaAl_xFe_{12-x}O_{19}$ (x=2, 4 and 6) samples. The XRD data analysis of the samples was done using computer software PCPDF Win, Powder-X and fullproof software suite. By comparing the patterns with JCPDS, the phases in the different samples are determined. It has been observed that all the observed lines match perfectly with the standard pattern and no extra lines were detected, hence it confirmed the single magnetoplumbite phase in the reported samples. The space group for the samples is observed to be SG: $P6_3/mmc$ (No. 194).

Lattice parameters (a & c), unit cell volume (V), X-ray density (ρ_X), bulk density (ρ_B) and porosity (P) of samples of NHFs were calculated from XRD data and their values are enumerated in Table 1.

The lattice parameter (a) and (c), unit cell volume (V), X-ray density (ρ_X) and Bulk density (ρ_B) increases with substitution of Al^{3+} ion in calcium hexaferrite sample. This is due to relatively small ionic radius of Al^{3+} ion (0.53 Å) comparing to that of Fe^{3+} ion (0.64 Å) for six fold coordination. As a result, the cell volume of calcium hexaferrite decreases with increase in the substitution of Al^{3+} ion. These results are in agreement with published results well to that reported by Ounnunkad and Winotai [11] . The similar trend of lattice parameters and unit cell volume was reported by Sang Won Lee *et al.* [12]. Rewatkar *et al.* [13] reported the similar values of lattice parameter a and c. Similar results were reported by Abdulmumeen Lohmaah *et al.*[14], Sabah M. Ali Ridha and Mohmmad A. Awad [15] and Sachin Kumar Godara *et al.* [16].

The particle size of the samples calculated by Debye–Scherrer equation are given in the table 1.

Dielectric Properties of the samples

The variation of dielectric constant carried out at the fix frequency of 1KHz for the aluminium substituted calcium hexaferrites are shown in Figure 3.

As the temperature increases, the dielectric constant of samples of NHFs increases slowly up to the particular temperature (T_t). This particular temperature (T_t) is known as the dielectric transition temperature (T_t). However, beyond the particular temperature (T_t), the dielectric constant were found to increase

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abruptly for all the samples. A similar trend of the dielectric constant for $Ca(CoAl)_xFe_{12-x}O_{19}$ was observed by Giriya [17]. The similar results were reported by Sunil Kumar *et al.* [18] for chromium substituted barium hexaferrite and by N. Christy *et at.* [19] for Cobalt and Zirconium the substituted Calcium hexaferrites . The value of T_t for each composition is given in Table 2.

The Curie temperature T_c are also included in the table for the purpose of comparison. It is seen that the dielectric transition temperature decreases with increase in the content of Al^{3+} ions in calcium ferrite. It is seen from the table that the values of T_t and T_c are in good agreement. This therefore indicates that the change in the behaviour of the dielectric constant with temperature may be due to a magnetic phase transition where the material becomes a paramagnetic. A simultaneous lowering of dielectric constant with increase in concentration of Al^{3+} ions in substituted calcium hexaferrites accompanied by an increase in the electrical resistivity are suitable trends for applications in the microwave devices.

CONCLUSION :

The aluminium substituted NHFs samples were synthesized by the sol-gel auto-combustion technique. The XRD data have confirm the formation of M-type hexaferrites and the values of lattice parameters a and c of the sample supports this confirmation. The particle size calculated by Debye-Scherrer formula shows that the synthesized samples are in the nanorange. The dielectric properties of the samples were improved by substitution of Al^{3+} for Fe^{3+} in calcium hexaferrites.

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Table 1: Structural parameters of $CaAl_xFe_{12-x}O_{19}$ Samples where x=2, 4 and 6.

Structural Parameters	x=2	x=4	x=6
Lattice parameter (a) in (Å)	5.8179	5.8088	5.8000
Lattice parameter (c) in (Å)	22.1353	22.1045	22.0759
Unit cell volume (V) in $(Å)^3$	648.837	645.909	643.120
X-ray density (ρ_X) in (gm/cm^3)	4.907	4.634	4.325
Bulk density (ρ_B) in (gm/cm^3)	2.685	2.454	2.205
Porosity (P) in (%)	46.25	47.81	49.16
Particle size in nm	2.41683	1.45028	4.80000

Table 2: Transition Temperature (T_t) and Curie Temperature (T_c) of aluminium substituted NHFs.

Compounds	Transition Temp. T_t (K)	Curie Temp. T_c (K)
$CaAl_2Fe_{10}O_{19}$	573	577
$CaAl_4Fe_8O_{19}$	533	535
$CaAl_6Fe_6O_{19}$	493	499

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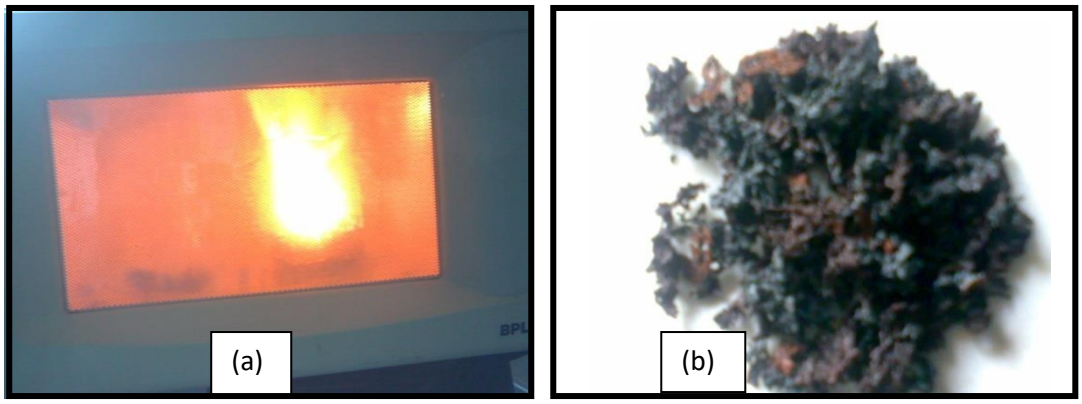

Figure 1(a) : Peak reaction stage in microwave oven (b)Ash obtained after combustion.

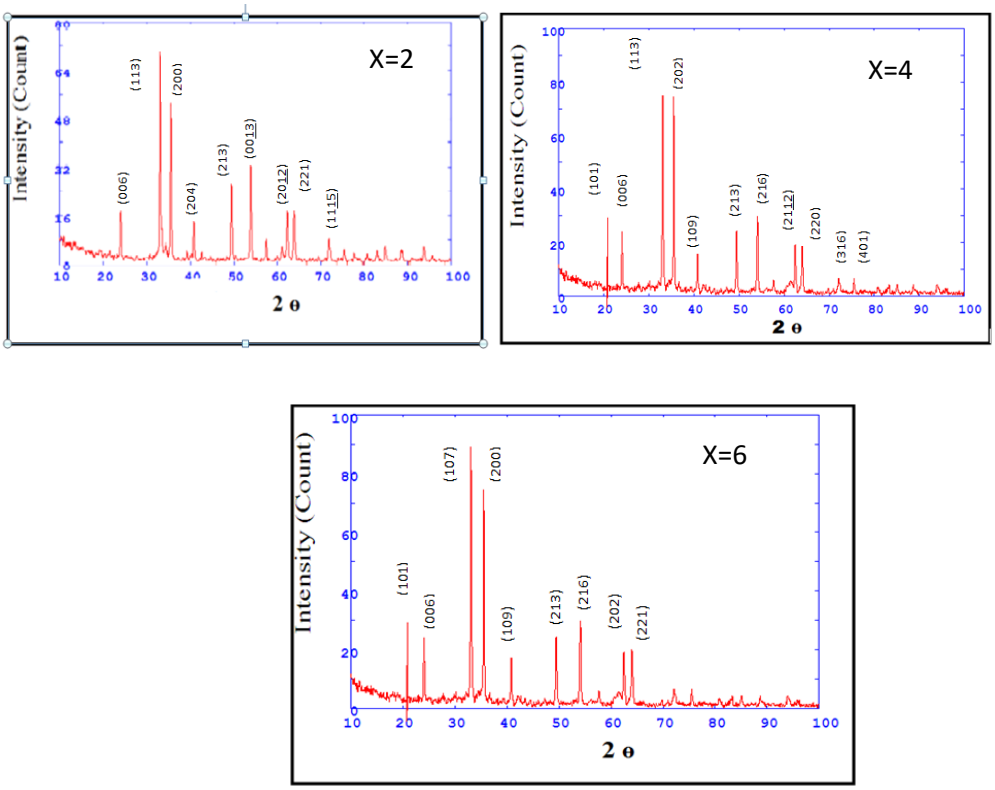

Figure 2: XRD patterns of $CaAl_xFe_{12-x}O_{19}$ samples where x=2, 4 and 6.

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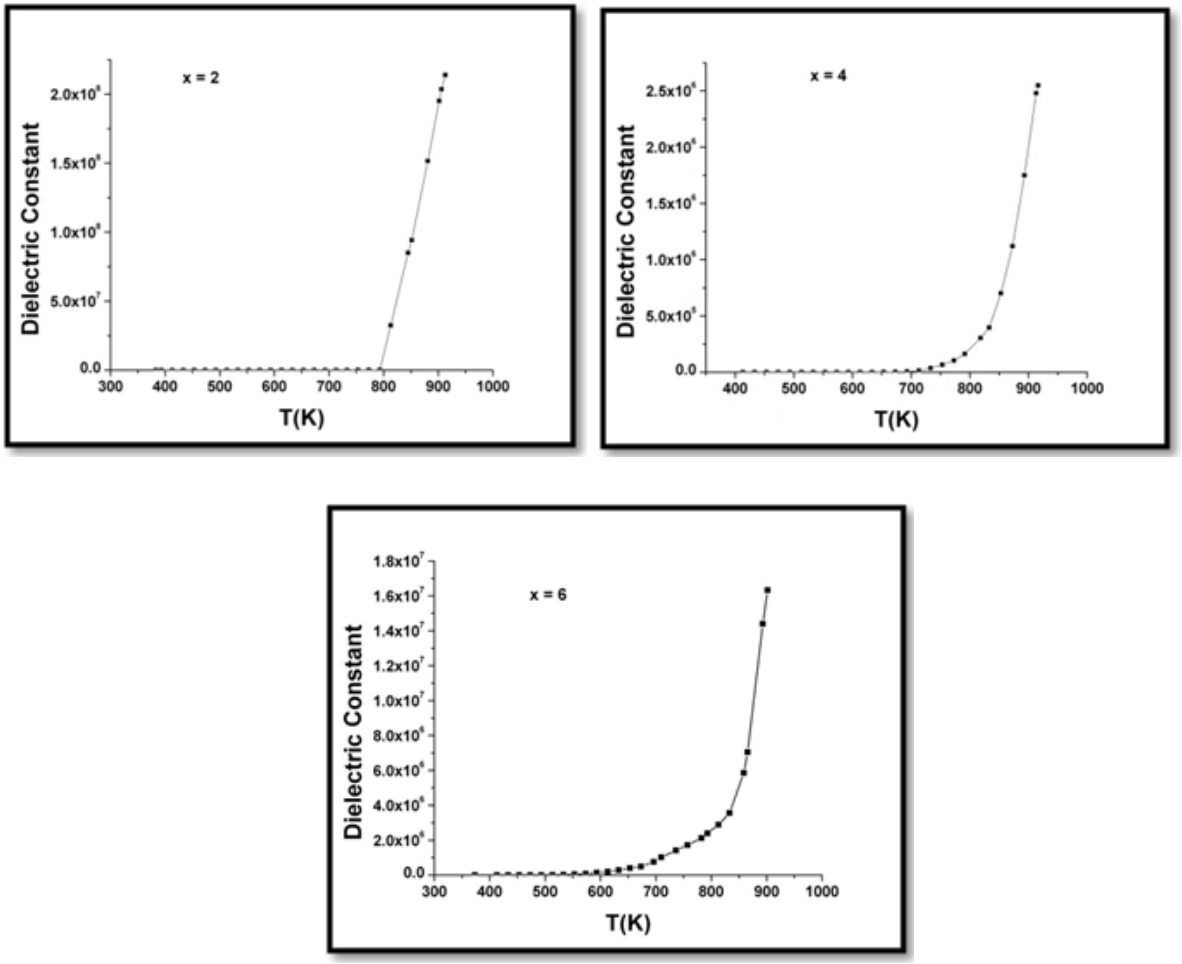

Figure 3 :Variation of Dielectric constant with temperature of $CaAl_xFe_{12-x}O_{19}$ with x=2 to x=6.

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