SYNTHESIS AND CHARACTERIZATION OF $CoFe_2O_4$ + $CaCu_3Ti_4O_{12}$ COMPOSITE OF FERRITE

A thesis submitted in partial fulfillment of the requirement

For the degree of

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IN

PHYSICS

By

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CERTIFICATE

This is to satisfy that the thesis entitled "**Synthesis and characterisation of CoFe$_2$O$_4$ + CaCu$_3$Ti$_4$O$_{12}$ composite of ferrite**" submitted by Smita Panda (Roll No.-410ph2137) & Ramesh Chandra Huika (Roll No.- 410ph2127) for the partial fulfilment of the requirements for the award of M.Sc. degree in Physics at National Institute of Technology, Rourkela, is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University or Institute for the award of a degree or diploma.

Date: Signature of the guide

Place: (D. Behera)

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<u>ACKNOWLEDGEMENT</u>

CANDIATES DECLARATION

We hereby declare that the project work entitled "**Synthesis and characterisation of CoFe$_2$O$_4$ + CaCu$_3$Ti$_4$O$_{12}$ composite of ferrite**", an authentic work carried by us, during the one year project at NIT, Rourkela, from July 2011 to May 2012 under the supervision of Dr.Dhrbananda Behera and is submitted for the partial fulfillment of the requirement for award of the degree of Master of Science in Physics to NIT, Rourkela. This has not been submitted anywhere else for the award of any other degree.

Date   SMITA PANDA

                                                                        RAMESH CHANDRA HUIKA

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ABSTRACT

Composite of cobalt ferrite ($CoFe_2O_4$) and CCTO are fabricated by chemical route method and its dielectric and structural properties are investigated. The composite powder fired at and above 800^0c and have perovskite structure. The composite then formed pellet and sintered at 900^0 C. It possess of both magnetic as well as dielectric property simultaneously. With X-ray diffraction, the phase transformation is confirmed. By the help of SEM characterization, the surface morphology of composite is confirmed. With EDAX images the percentage of elements in composite is also confirmed. Its dielectric properties have been studied in the temperature range 300-700 K. It is found that dielectric constant (ε) increases with increase in temperature. The dielectric loss increases with increase in temperature, irrespective of CCTO transition temperature, that ensures the semiconducting nature or thermally activated mechanism of conduction in the composites.

CHAPTER 1

1.1 INTRODUCTION

Ferrites are magnetic oxides of iron with other metal such as cobalt, nickel, zinc, barium, manganese and strontium. The ferrite core is produced by different ceramic process. So these are hard and brittle .Ferrites is generally two types namely hard and soft. Hard ferrites are again produced in two types, they are isotropic and anisotropic. The isotropic ferrite materials produced by without orientation; in any direction of applied magnetic they can be orient. But anisotropic ferrite materials depend on direction of applied magnetic field. [1] Cobalt ferrite is a hard magnetic material. The ferrite has remarkable properties such as high saturation magnetization, high coercivity, strong anisotropy along with good mechanical hardness and chemical stability Cobalt ferrite is ferrimagnetic with a high curie temperature of 793 K [2]. It is to be predicted to half metallic [3] .Cobalt ferrite can be used in giant magnetoresistance (GMR) devices and it good conducting for recording media [4].The high magnetostrictive cobalt ferrite is used in sensor application. Cobalt ferrite is widely used in magnetic resonance imaging (MRI), drug targeted therapy, bioactive molecule separation such as enzyme and protein [5].

Dielectric material is defined as an ideal insulator, which has no free electrons. A dielectric material has interesting properties because it has ability of electric field to polarize the material to create electric dipoles. High dielectric constant materials are much interest because in their miniaturization of electronic devices. $CaCu_3Ti_4O_{12}$ (CCTO) has generally interest owing to its high giant dielectric constant despite by its centrosymmetric nature [6]. Polycrystalline CCTO was to exhibit remarkably high dielectric constant $>10^4$ at 100 KHz at 300 K. However these properties are strongly depending on processing method .The dielectric constant of a single crystal is reported as 10^5. Further it was reported that dielectric constant is constant remain constant for temperature of range 100-400 K [7]. However, its decrease three times as temperature is below 100 K [8]. Dielectric materials have used in capacitors. Liquid dielectric also employed as electrical insulators it has ability insulate coils of transformer both electrically and thermally.

1.1.1 <u>History of magnetism</u>:

The writings of Thales, the Greek, establish that the power of loadstone, or magnetite, to attract iron was known at least as long as 600 B.C. It has claimed that Chinese used compass before 2500 B.C.

1.1.2 <u>M a g n e t i c   p r o p e r t i e s</u>:

1.1.2.1 <u>Magnetism:</u> It is a statement by which one material applies either attractive or repulsive force on other material. The source of magnetic force is moment of electrically material. In an atom the electron has planetary motion due to which they go round the nucleus. This orbital & own spin motion of electron causes separate magnetic moments, which contribute to the magnetic behaviour of materials.

Magnetic are found to exist in magnetic materials, and it is analogous to electric dipoles. A magnetic dipole is a small magnet composed of north and south poles. Within magnetic field, the forces of field apply a torque that tends to orient the dipoles with the field.

1.1.2.2 <u>Magnetic field</u>:

If a magnetic field is generated by passing current "I " through a coil of length L and numbers of turns n, then the magnetic field strength, H(units A/m), is given by

$$H = nI / L$$

Magnetic flux density (induction) is the measure of lines within a medium. It has unit as weber (Wb)/m^2 or tesla and is defined as

$$B = \mu H$$

Where μ - permeability. It is a specific property of the medium, and it has unit as Wb/A.m or henry (H)/m.

Relative magnetic permeability, is define as

$$\mu_r = \mu/\mu_0$$

μ_r is a measure of the degree to which the material can be magnetized.

Where μ_0 – magnetic permeability of vacuum.

If M- magnetization defined as M, is defined as $M = \chi_m H$ then

$$B = \mu_0 H + \mu_0 M = \mu_0 \mu_r H$$

X_m is called the magnetic susceptibility and given as

$$X_m = \mu_r - 1$$

Types of magnetism:

It is depends on the material's magnetic susceptibility – its magnitude and sign.

Three basic magnetism are:

- ➢ Dia-magnetism
- ➢ Para-magnetism
- ➢ Ferro-magnetism.

1.1.2.3 Dia-magnetism

It is very weak in nature and it exists only in presence of an external field, and it is non-permanent. It applied external field acts on atoms of a material, slightly unbalancing their orbiting electrons, and creates small magnetic dipoles within atoms which oppose the applied field. The action produces a negative magnetic effect known as diamagnetism. Its magnetic moment is small, and the magnetization (M) direction is opposite to the direction of applied field (H).

1.1.2.4 Para-magnetism

It is slightly stronger when an external field is applied dipoles line-up with field and it brings in a positive magnetization. However, the dipoles do not interact. Materials which exhibit a small positive magnetic susceptibility in the presence of a magnetic field are called Para-magnetic, and the effect is termed as Para-magnetism. In the absence of an external field, the orientation of atomic magnetic moments is random leading to no net magnetization. When an external field is applied dipoles line-up with the field, resulting in a positive magnetization. However, because the dipoles do not interact, extremely large magnetic fields are required to align all of the dipoles. In addition, the effect is lost as soon as the magnetic field is removed.

1.1.2.5 <u>Ferro-magnetism</u>

Both dia and paramagnetic materials are considered as non magnetic because they exhibit magnetization only in presence of an external field. Certain materials contain permanent magnetic moments even in the absence of an external field. This is result of permanent unpaired dipoles formed from unfilled energy levels. These dipoles can easily line-up with the imposed magnetic field due to the exchange interaction or mutual reinforcement of the dipoles. These are chrematistics of *ferromagnetism*. Materials with ferromagnetism (Fe,Co,Ni,Gd) possess magnetic susceptibilities approaching 10^6.

Frome the above temperature, ferromagnetic materials behave as paramagnetic materials and their susceptibility is given by the Curie-Weiss law.

Defined as

$$Xm = C / (T\text{-}T_c)$$

Where C–material constant, T – temperature, T_c – Curie temperature.

Ferro Magnets are very strong dipoles line-up permanently upon application of external field. Have two sub-classes:-

    1. Anti ferromagnetism:

    2. Ferrimagnetism:

1.1.2.6 <u>Anti ferromagnetism</u>

In Anti ferromagnetism, Dipoles are line-up, but in an opposite directions, as a result there is no magnetization. The Exchange interaction which is responsible for parallel alignment of spins is extremely sensitive to inter-atomic spacing and to the atomic positions. Due to this sensitivity it causes anti parallel alignment of spins. When the anti parallel spin magnetic moment strength is equal, there is no net spin moment exists, and as a result susceptibilities are quite small. In continuous observation anti ferromagnets, they attain maximum susceptibility at a critical temperature called *Neel temperature*. Above Neel temperature, antiferro magnets become paramagnetic.

1.1.2.7 <u>Ferri magnetism</u>

Some ceramic materials exhibit net magnetization

• Below the Neel temperature, therefore, ferromagnetic materials behave very much like ferromagnetic materials and are paramagnetic above the Neel temperature.

• These materials exhibit a large but field dependent magnetic susceptibility similar to Ferro-magnets.

They also show Curie-Weiss behaviour. As these ceramics are good insulators, electrical losses are minimal, and hence ferrites have lot of applications in devices such as high frequency transformers.
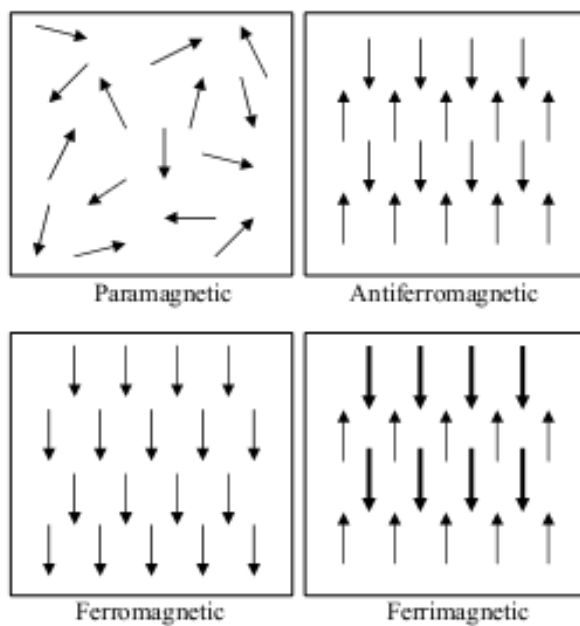

Fig 1.1.2 Different types of magnetism.

1.1.3 <u>Classification of Ferrimagnetic materials</u>
1. Soft ferrites
2. Hard ferrites

1) **Soft ferrites** :

Soft ferrites are characterizes by low corecivity and high magnetic permeability. These are easily magnetized and demagnetized .They exhibit small hysteresis losses. Examples of soft ferrites are superalloy, MnZn ferrites, NiZn ferrites etc. These materials great applications in electrical industry such as manufacture of transformers, generators, electric motors.

2) **Hard ferrites**:

Hard ferrites are characterizes by high remnant induction and high corecievitis. Generally they exhibit large hysteresis losses .Examples are Co Steel, Cobalt ferrites .Ferrimagnetism was first found in materials with the spinel crystal structure. Their chemical formula is PQ_2X_4 in which often $X=O^{2-}$, $Q= Fe^{3+}$ and P is a some divalent cation. Ferrate is defining here as any ferrimagnetic material with low electrical conductivity [9]. All most all of the known ferrimagnetic material is their poor conductor of electricity. Exception including some inters material compounds such as Mn_4N. by far the best conductor among those we called ferrate is magnetite. This is a spinel. Its resistivity at room temperature is approximately 7×10^{-3} ohm cm. the critical temperature above which the spontaneous magnetization of a ferrimagnetic vanishes. It has been called the Neel temperature.

Curie temperature because there is spontaneous magnetization and Neel temperature because the order is not parallel. Hard ferrites are many applications such as horse power motor, automobiles, audio and video recorders etc.

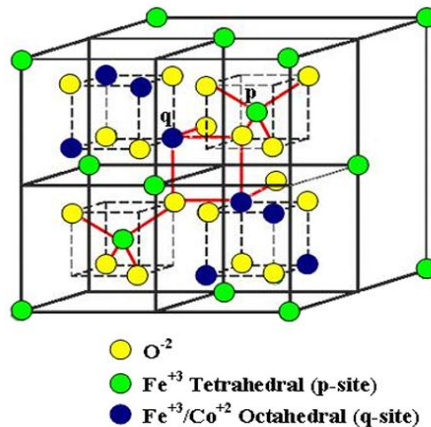**1.1.4 Structure of cobalt ferrite**:

○ O^{-2}
● Fe^{+3} Tetrahedral (p-site)
● Fe^{+3}/Co^{+2} Octahedral (q-site)

Fig.1.2 Structure of $CoFe_2O_4$

1.1.5 Magnetic properties in cobalt ferrite:

Magnetic nanoparticles have been the topic of intense research because of its potential applications in high density magnetic recording. Among the various ferrite materials cobalt ferrite ($CoFe_2O_4$) has been widely studied because of its having excellent chemical stability and good mechanical hardness [10]. By controlling the composition and structure of $CoFe_2O_4$, the success of its practical application relies on the capability of controlling crystal size within the super-paramagnetic and single domain limits [11]. Cobalt ferrite is a hard magnetic material along with high coercivity and moderate magnetization, along with large magnetic anisotropy. Due to these properties with great physical and chemical stability, make cobalt ferrite suitable for various application like audio and videotape and high-density digital recording disks etc [12]. A system of non-interacting single domain particles suggests that $coFe_2o_4$ nanoparticles exhibit an effective uniaxial anisotropy. And the coercivity of ferrite powder strongly depended on the annealing temperatures and can be directly related to the variation of cobalt ferrite particles sizes.

1.1.6 Dielectric material:

A dielectric material has interesting electrical properties because of the ability of an electric field to polarize the material to create electric dipoles. A dipole is an entity in which   equal positive a negative charges are separated by a small distance, the electric dipole moment is given by the relation

$$\mu = q \times dl$$

Where q is charge and dl is separation distance .The electric dipole is a vector quantity.

If C_0 is the capacitance of the condenser with the region between the conductors evacuated and C is the capacitance when the region is filled with dielectric. This ratio is

$$C/C_0 = \epsilon_r$$

It is found to be independent of the shape of the conductor. And it is solely a characteristic of the particular dielectric medium used. ϵ_r is the relative permittivity of the medium. ϵ_0 is called permittivity in vacuum. The dielectric constant of a material is a microscopic quantity that measure how effective an electric field is in polarizing the material.

1.1.7 <u>Classification of dielectric material:</u>

Dielectric polarization is nothing but displacement of charge particle under the action of the electric field to which they are subjected. They are classified on the basis of electric dipole moment in atoms, ions or molecules of the material.

The important polarizations are
1. Electronic polarization
2. Ionic polarization
3. Orientation polarization

1.1.7.1 .<u>Electronic polarization</u>:

Electronic polarization is defined as the dipole moment per unit volume. This is given by the relation:

$$\mu_e = \alpha_e E$$

Where is α_e called electronic polarisability.

Thus the induced dipole moment is proportional to the applied field.

1.1.7.2 .<u>Ionic polarization</u>:

When the atoms form molecules electronic polarization is still possible there may be additional polarization due to a relative displacement of the atomic component of the molecule in the presence of an electric field. Ionic polarisability is given by the relation

$$\mu_i = \alpha_i E$$

Where α_i is called ionic polarzibility constant.

1.1.7.3 <u>Orientation polarization</u>:

This type of polarization only occurs in polar substances. The permanent moment is purely a matter of molecular geometry. The permanent molecular dipoles in this type of materials can rotate about their axis of symmetry to a line with an applied field which exert a torque in them. This additional polarization effect is accounted by an orientation term α_0.

1.1.8 <u>Static dielectric constant of solids and liquids:</u>

The three classes of material may be identified as far as dielectric behaviour of solids concerned.

1. Solids exist only electric polarizability is called elemental solid dielectrics.
2. Solids which manifest electric & ionic polarizabilities are called ionic non polar dielectrics.
3. Solids which possess orientation as well as ionic and electronic polarizability are called polar solids.

1.1.9 <u>Ferroelectric maaterials:</u>

Below a certain temperature it is found that some materials spontaneously occur an electric dipole moment. Just as with ferromagnet crystals exhibit a hysteresis curve P-E. It can be explained by a domain hypothesis.

When an electric field is applied to a ferroelectric crystal, first the polarization rises rapidly with applied field to a value which dependence is linear. Linear extrapolation to zero fields gives spontaneous polarization. The existence of a dielectric hysteresis load in a dielectric material implies that the substance possess a spontaneous polarization and the value of polarization depends upon the dimension of a specimen the temperature, the texture of crystal, the thermal & electric properties of the sample. The ferroelectric hysteresis loop of a material changes its shape as the temperature rises. The height and width decrease with increase in temperature. At a particular temperature called as ferroelectric Curie temperature.

While the most dielectrics are only weakly anisotropic, weakly non linear and weakly sensitive to electromechanical effects, mechanical strain are still large enough to be of practical value in an electrical driven acoustical resonators. The entire phenomena of elctromechanical phenomena are called piezoelectricity.

When a dielectric material is subjected to an alternative field the orientation of dipoles and hence the polarization will tend to reverse every time the polarity of field changes. When the frequency is increased the dipoles no longer be able to rotate sufficiently so there oscillation will begin to leg behind those of field. This lead to fall in permittivity of dielectric material with increase in frequency usually referred to anomalous dielectric dispersion. [16]

1.1.10 structure of CCTO ($CaCu_3Ti_4O_{12}$):

CCTO is cubic ABO_3 pervoskite type in which Ca^{2+} and Cu^{2+} share the A-site .The size difference between Ca^{2+} and Cu^{2+} causes the TiO_6 octahedral to undergo substantial tilting leading to a body centred cubic super all of space group Im_3 in which the Ti^{4+} ions occupies centrosymmmetric position in the octahedral sites .The angle of tilting is sufficiently large that Cu^{2+} ions occupy an essentially square-planner environment [13].
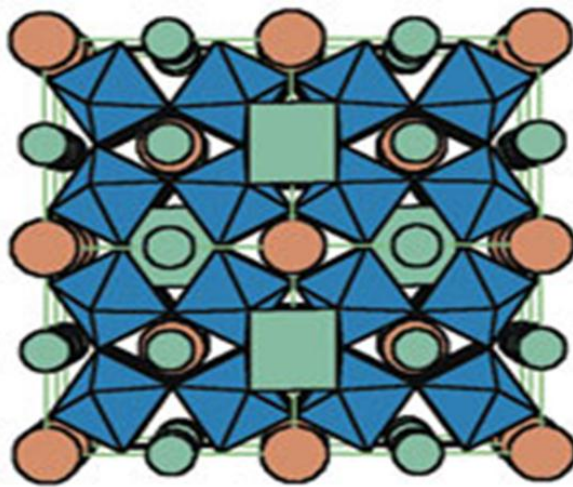

Fig 1.1 Crystal structure of CCTO [14]

Green spheres = Cu

Blue octahedral = TiO_6 units

Brown spheres = Ca

Green square = CuO_4 planner units

1.1.11 Dielectric properties of CCTO

As per the research we found that the perovskite-related body-centered cubic materials $CaCu_3Ti_4O_{12}$ (CCTO) exhibited not only in giant dielectric constant at room temperature ($\varepsilon' \approx 10^4 - 10^5$) but also a nearly constant dielectric constant between 100 and 400 K. [11-15]. These properties are very important for device implementation and to make the CCTO a promising material for microelectronic application. From the structural studies we found that CCTO maintains a cubic structure without phase transitions. The nature and characteristics of the giant dielectric constant of CCTO ceramic remain unsolved.

CHAPTER 2

2.1 LITERATURE SURVEY:

2.1.1 L.C Kretley et al.,microwave and optical technology letters.2,39(2003)

By using polymeric citrate precursor route the Commercial oxides Ca $(OH)_2$, $CaCO_3$ and TiO_2 were used in CCTO preparation the material was grounded on a Fritsch. Pulvesette 6 planetary mill with a proportionality amount of Ca $(OH)_2$.$3H_2O$ $4TiO_2$. Milling was performed in sealed stainless steel for 1 hour. The powered was mixed with an organic birder and compared to disc at a pressure of 20 MPa. Pellets are sintered at 1050^0 C for 24 hour. The reaction as follows [18]

Ca $(OH)_2$ + 3CuO+ $4TiO_2$ $\rightarrow$ $CaCu_3Ti_4O_{12}$+H_2O

2.1.2 Li Then Mei et al., J.American Ceramic Societties .91, 11(2008)

CCTO specimen was prepared using a conventional solid state reaction method and sintering process. The CaCO (99.95 %), CuO (99.7%), TiO_2 (99.9%) the powder and calcinated for two hour at 960^0 C and sintered for 12 hour. The powder was uniaxial pressured at 75 MPa. The samples were characterized by XRD, XPS and dielectric measurement. [19]

2.1.3 B.Bbarbier et al.,Journal of Jeuceramics (2008)

In co-precipitation method, Metal chloride ($CaCl_2$, $TiCl_3$, $CuCl_2$) were dissolved in water. Then poured in oxalic acid used as precipitation agent. Precursors were calcinated in air at 950 ^{0} C for 10 hour. Finally CCTO powder was obtained. [20]

2.1.4 Deepam Maurya et el., Bull material Sci.(2008)

For preparation of CCTO powder, sol-gel technique is used .Tiatnum butoxide ($TiOC_4H_9$) was mixed with acetic acid and stirred for 30 min. inside a glove box with control humidity. Calculated amount of precursors Calcium acetate and mono hydride cupper acetate were mixed with 15ml of acetic acid and 15 ml of ethanol and stirred for 30 min. 10 ml of 2-methy ethanol was added and the solution stirred at 100^0 C FOR 30 min. and then cooled at room temperature. Lastly light transparent sol was obtained. [21]

CHAPTER 3

3.0 <u>EXPERIMENTAL DETAILS:</u>

3.1 <u>Materials required cobalt ferrite</u>

For preparation of cobalt ferrite the required weights of $(CH_3COO)_2CO.4H_2O$ and $Fe(OOCCH_3)_2$ salts were dissolved in distilled water to produce a solution with Fe:Co mole ratio of 2:1. All reagents were of analytical grade and were used without further purification.

3.2 <u>Synthesis of cobalt ferrite</u>

The materials used for this method of preparation was cobalt acetate tetra hydrate $(Co (CH_3 COO)_2. 4H_2O)$, ferric acetate anhydrous $(Fe (CH_3COO)_2)$ and citric acid $(C_6H_8O_7 .H_2O)$. Cobalt acetate, ferric acetate and citric acid powders were mixed by 1:2:3 molar ratios with acetone. Then the powders (with powder to ball weight ratio 1:5) were milled in a mini ball mill using agate balls and stainless steel container of 200 ml under air atmosphere using with 3 mm balls at 400 rpm milling speed for 2 hrs. The ball milled powder was calcined in air at 800° C for three hours to get Cobalt ferrite $(CoFe_2O_4)$.

3.3 <u>Materials required for CCTO</u>

For preparation of CCTO the required weights of $Cu (NO_3)_2.3H_2O$, $Ca(NO_3)_2.4H_2O$, and TiO_2 were dissolved in distilled water to produce a solution of Ca:Cu:Ti mole ratio of (1:3:4). All reagents were of analytical grade and were used without further purification   .

3.4 <u>Synthesis of CCTO</u>

For synthesis of CCTO powder, we adapted semi sol-gel method. Calculated amount of calcium nitrate tetrahydrate $(Ca (NO_3)4H_2O)$, copper nitrite trihydrate $(Cu (NO_3)_2.3H_2O)$, titanium dioxide (TiO_2) were dissolved in stoichiometric ratio 1:3:4 in deionized water. The solution is homogenized in magnetic stirrer on the hot plate 2 hrs. Still sol is formed. The
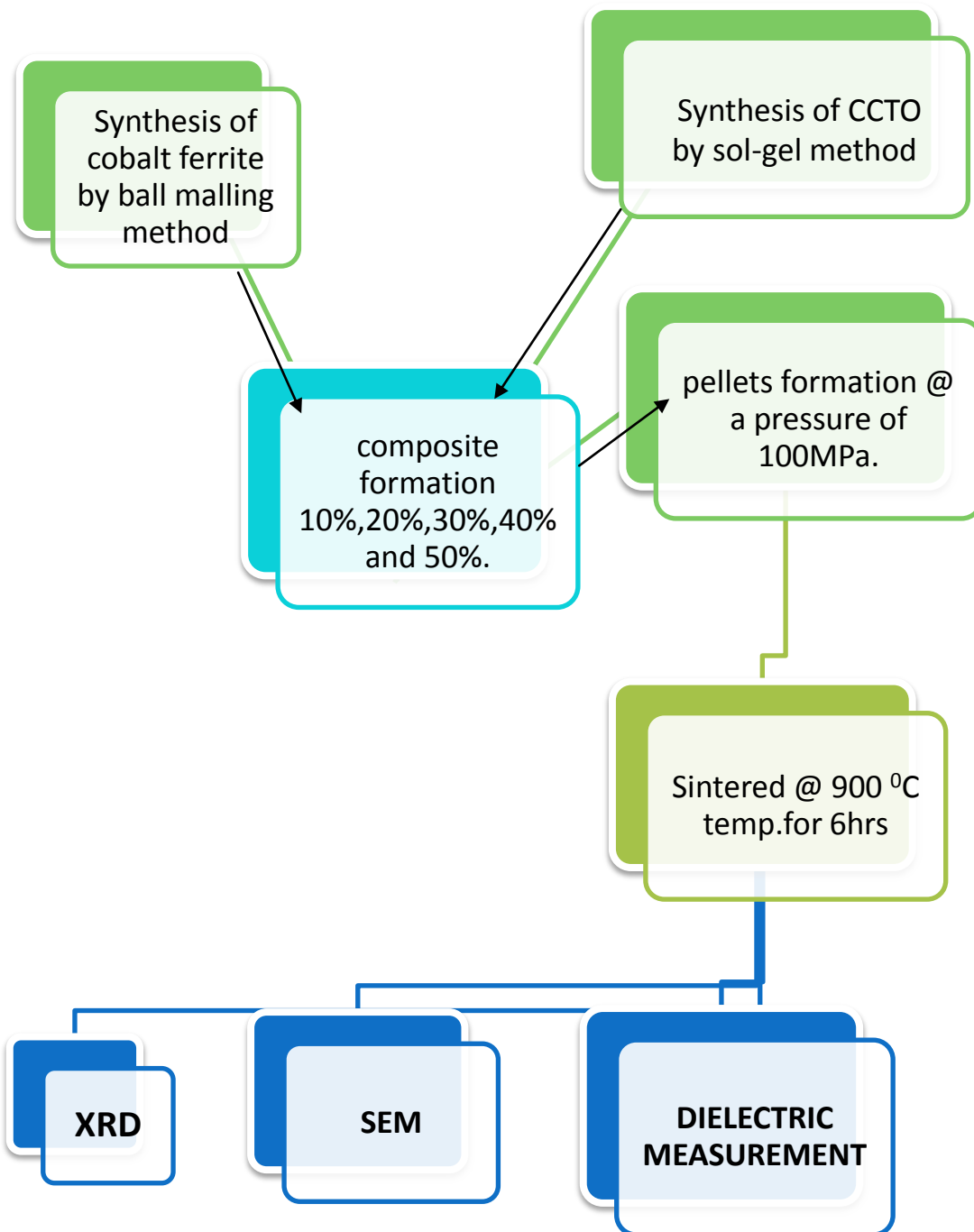
solvent is evaporated directly on hot plate at temperature (75-100) until thick jelly was formed. Teflon coated bar magnet and hot late used for evaporation water from solution by continuous string. Again jelly like material heated with high temperature for removal of water. Finally we got black powder; this powder is calcined at temperature 580^0 C for 6 hrs. Obtain powders are grounded for 2 hrs**.**

3.5 <u>Composite formation ($CoFe_2O_4$ and CCTO):</u>

1. $CoFe_2O_4$ +10% CCTO
2. $CoFe_2O_4$ +20% CCTO
3. $CoFe_2O_4$ +30% CCTO
4. $CoFe_2O_4$ +40% CCTO
5. $CoFe_2O_4$ +50% CCTO

The composite is obtain by adding different composition of CCTO of 10%, 20%, 30%, 40%, 50% to cobalt ferrite powder. The pellets are formed at pressure of 100 MPa. Pelletes are sintered at 900^0 C temperatures for duration of 6 hours. All the synthesized samples were characterised for structural and phase formation confirmation undergoes by using powder x-ray diffracometrer. The surface morphology and compositional analysis is done by scanning electron microscope. The dielectric measurements of samples are done by using HIOKI3532-50LCR Hi Tester.

3.6 Flow chart for COMPOSITE (CoFe$_2$O$_4$+ CCTO):

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┌─────────────────┐          ┌─────────────────┐
│  Synthesis of   │          │ Synthesis of CCTO│
│  cobalt ferrite │          │ by sol-gel method│
│  by ball malling│          └─────────────────┘
│     method      │                    │
└─────────────────┘                    │
         │                             │
         ▼                             ▼
    ┌──────────────────┐      ┌──────────────────┐
    │    composite     │─────▶│ pellets formation @│
    │    formation     │      │  a pressure of   │
    │ 10%,20%,30%,40%  │      │    100MPa.       │
    │    and 50%.      │      └──────────────────┘
    └──────────────────┘               │
                                       ▼
                              ┌──────────────────┐
                              │ Sintered @ 900 $^0$C│
                              │  temp.for 6hrs   │
                              └──────────────────┘
                                       │
              ┌────────────────────────┼────────────────────────┐
              ▼                        ▼                        ▼
          ┌───────┐              ┌───────┐              ┌──────────────┐
          │  XRD  │              │  SEM  │              │  DIELECTRIC  │
          └───────┘              └───────┘              │ MEASUREMENT  │
                                                        └──────────────┘
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3.7 <u>Characterization Techniques:</u>

All the samples were characterised by various techniques such as X-Ray diffraction (XRD), Scanning electron Microscope (SEM) with Elemental detection analytical X-ray (EDAX) and dielectric measurement. X-ray diffraction pattern were recorded on a PAN analytical diffractometer (PAN-PW 1830) using Ni filtered Cu K_α ($\lambda = 1.541A°$) radiation within the 2θ range from 20^0 to 80^0 at a rate of 2^0 per minute. The scanning electron micrographs were recorded using a JEOL-JSM-6390LV scanning electron microscope operating at an acceleration voltage of 10 and 20 KV

3.7.1 <u>X-ray diffraction</u>:

In nanoparticle research, X- ray diffraction patterns have been widely used for obtaining the critical features such as crystal structure, crystallite size, and strain. Except for single crystalline nanoparticles, the randomly oriented crystals in nanoparticles cause broadening of the diffraction peaks. X-ray diffraction method is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.

<u>Fundamental principles:</u>

It is based on constructive interference of monochromatic X-rays and a crystalline sample. Cathode ray tube generated these X-rays that are filtered to produce monochromatic radiation which is collimated to concentrate and directed to the sample. The incident rays interact with the samples and produces constructive interference when conditions satisfy Bragg's law i.e.

$$n\lambda = 2d \sin \theta$$

Where, d = perpendicular distance between lattice planes of miller indices, λ= wavelength of the incident, θ = glancing angle, n = an integer- 1, 2, 3… etc

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. Then X-rays are detected, further processed and counted. With the help of scanning the sample through a range of 2θ angles, all the possible diffraction directions of the lattice should be attained due to random orientation of the powered material. Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing. This is achieved by comparison of d-spacing with standard reference patterns.

3.7.2 <u>Scanning electron microscope (SEM):</u>

A SEM (Scanning Electron Microscope) can be utilized for high magnification imaging of almost all materials. The surface morphology of the sample was investigated using JEOL JSM-5300 microscope (acceleration voltage 15 KV). On a carbon tape the sample powder were deposited before mounting on a sample holder for SEM analysis. The types of signals produced by a SEM include secondary electrons, back scattered electron (BSE), characteristic x-ray transmitted electrons etc. SEM produces high resolution images of sample surface.

The SEM is a type of electron microscope that helps in forming various images of the sample surface by scanning. The high energy electron beam interacts with the surface of sample and generates a signal. SEM images have greater depth of field (curved surfaces are resolved properly) yielding a characteristic 3D appearance useful for understanding the surface structure of a sample. Magnification is of order 10,000 X and resolution 10 nm.

The main use of EDAX is to accurately determine the composition of the sample which is under observation. On the other hand, the electron microscopic images provide the real time pictures of the size and morphology of the nanoparticles, the EDAX analysis provides the exact composition of the sample. When the samples are exposed to high energy electron beams, the various atoms present in the sample emits characteristics X-rays, which are then observed as several distinct peaks on an energy scale. The intensities of the peaks are compared with the peaks of a standard sample to obtain the relative amounts of each atomic species and thus determine the accurate composition of the sample.

3.7.3 <u>DIELECTRIC MEASUREMENTS</u>:

3.7.3.1 <u>Dielectric Constant Measurement</u>

Ferroelectric ceramics are dielectric whose electrons are bound to the nucleus by strong forces and hence they are not free under the influence of an external field. The molecules may be represented as positive nuclei of charge q surrounded by a symmetrically distributed negative electron cloud of charge – q. The centres of gravity of the positive and negative charge distributions coincide in the absence of an applied field. The positive and negative charges experience electric forces when the molecules placed in an external field, tending to move them apart in the direction of the applied field. The distance moved is very small (10-10 m) as the displacement is limited by restoring forces which increases with the increase in

displacement. The molecules are said to be polarized, when the centres of positive and negative charges no longer coincide. Now each molecule forms a dipole whose moment is defined as μ = q dx, where dx is distance between the two centres of the charges and is a vector pointing from the negative to the positive charges. In ferroelectric ceramics a spontaneous polarization can exist even in the absence of an applied electric field. Ferroelectric can thus be used as a capacitor. Owing to the polarization of the medium, charges are induced at the surface of the dielectric.

Ferroelectric ceramics generally have much higher dielectric constants, typically several hundred to several thousand. It is calculated from the measured capacitance values of the samples using the formula:

$$C = K \, \varepsilon_0 \, A \, /d$$

Where,   C: Capacitance

      K: dielectric constant

      A: area of the electrode

      ε_0: permittivity of the free space

The dielectric measurements in the present study were done using HIOKI 3532-50LCR HiTester. Frequency vs. dielectric constant graph was obtained by plotting frequency in X-axis and dielectric constant in Y-axis.

3.7.3.2 <u>Dielectric loss</u>

When a dielectric material is subjected to an alternating field the orientation of the dipole changes and hence the polarization will tend to reverse every time the polarity of the field changes. As long as the frequency remains low (<106 c/sec), the polarization follows the alternations of the field without any significant lag and the permittivity is independent of frequency and has the same magnitude as in a static field. The dipoles will no longer be able to rotate sufficiently rapidly when the frequency is increased, hence their oscillations will begin to lag behind those of the field. When the frequency is further raised the permanent dipoles, if present within the medium, will be completely unable to follow the field and the contribution to the static permittivity from this molecular process i.e. orientation polarization ceases. This usually occurs in the ratio frequency range (106 – 1011 Hz) of the electromagnetic spectrum. At still higher frequencies, usually in the infra-red (1011 – 1014 Hz) the relatively heavy positive and negative ions cannot follow the field variation so that

the contribution to the permittivity from the atomic or ionic polarization ceases and only the electronic polarization remains. The above effects lead to fall in the permittivity of a dielectric material with increasing frequency. When the period of the applied voltage is much larger than the relaxation time of a polarization process, polarization is essentially complete at any instant during each cycle. The charging current is 90 degree advance in relation to the voltage so that no electrical energy is lost during charging. When the period of the applied voltage is much shorter than the relaxation time for a polarization process, the polarization does not occur at all. Here again, the charging current is 90 degree advanced of the applied voltage. When the period is in the same range as the relaxation time, resonance occurs. At resonance, current leads the voltage by (90-δ) where δ is loss angle and tan δ is a measure of the electrical loss due to resonance. The electrical loss at low frequencies is mainly due to d.c. resistivity but at high frequencies the electrical loss is mostly due to dipole rotations or due to ionic transitions from the lower energy states. Because of the upward transition the energy is absorbed from the applied field. The losses which fall on the infrared region are referred to as infra-red absorption and in the optical region are referred to as optical absorption.

With alternating voltage, the charge stored on a dielectric has both real (in phase) and imaginary (out of phase) components, due to either resistive leakage or dielectric absorption. The loss is expressed by the ratio of out of phase component to the in phase component. This is D, the dissipation factor of the dielectric loss, also frequently called loss tangent tan δ. It is measured directly using HIOKI 3532-50LCR Hi tester.

CHAPTER 4

4.0 Result and Discussion:

4.1 XRD Analysis:
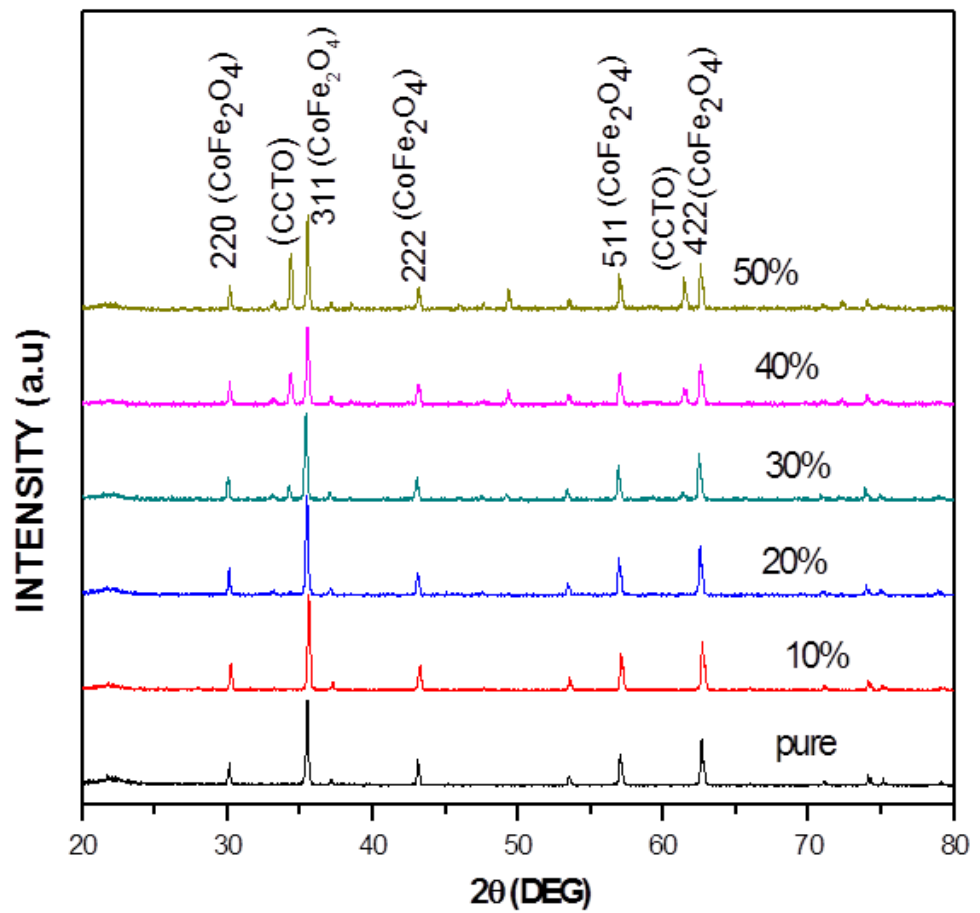
Fig 4.1 (a): XRD data of $CoFe_2O_4$ and CCTO at different composition.
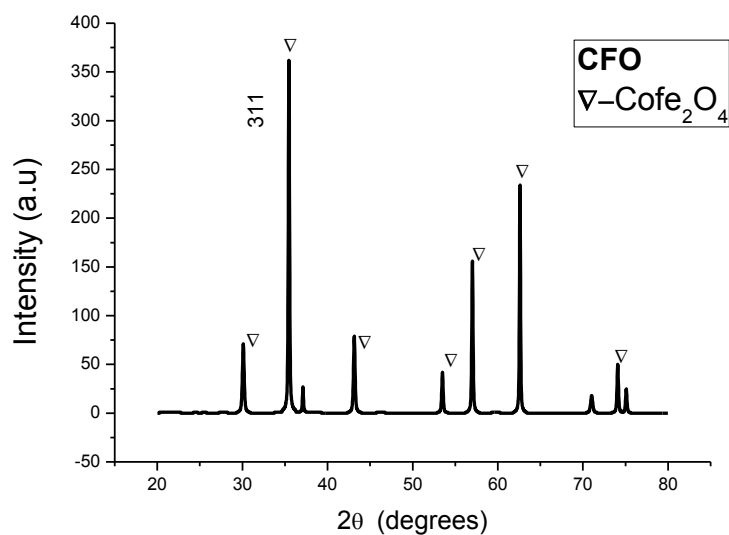
Fig 4.1 (b) XRD data of pure form of cobalt ferrite.
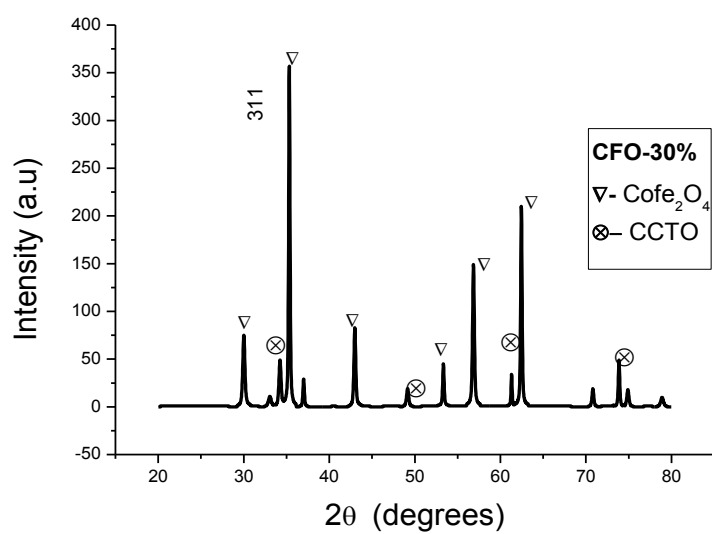
Fig 4.1 (c) XRD data of cobalt ferrite and 30% CCTO
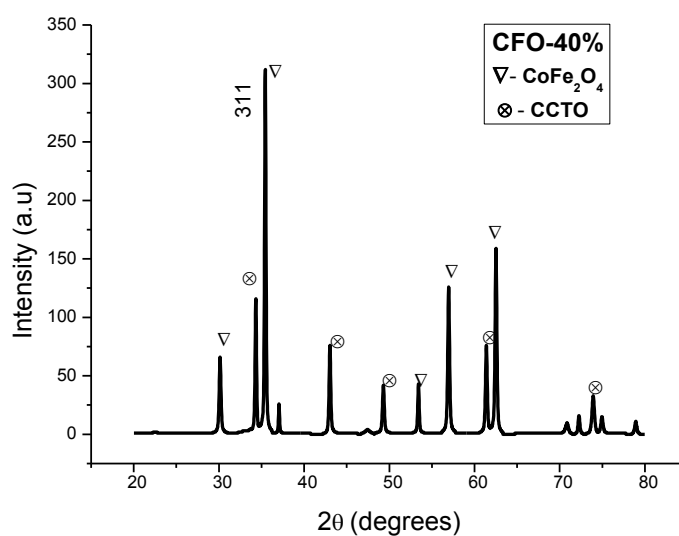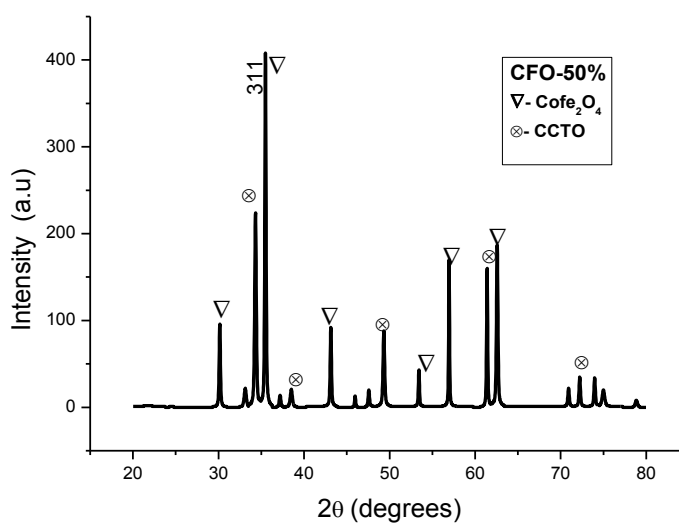
Fig 4.1 (d) XRD data of cobalt ferrite and 40% CCTO

Fig 4.1 (e): XRD data of cobalt ferrite and 50% CCTO

All the samples X-ray diffraction pattern were recorded on a PAN analytical diffractometer (PAN-PW 1830) using Ni filtered Cu Kα (λ = 1.541A°) radiation within the 2θ range from 20^0 to 80^0 at a rate of 2^0 per minute represents the X-Ray diffraction spectra of composite prepared by sol-gel method. XRD pattern of 800^0 C the Cobalt ferrite with CCTO samples are shown. The 2θ value of cobalt ferrite sample was found to match with JCPDS − 76-0144. Similarly the 2θ value of CCTO sample was found to

match with JCPDS – 84-0311. Above graphs, at (311) plane at 35^0 C, the prominent peaks in XRD plot indicates that various (hkl) miller indices planes of cobalt ferrite with CCTO Composites. The samples calcinated at $850\ ^0$C many extra peaks other than cobalt ferrite with CCTO phase. The literature survey of Cobalt ferrite with CCTO relates impurity peaks. The X-Ray diffraction spectra confirm single phase perovskite structure. From fig 4.1(a) at (311) plane, maximum intensity of cobalt ferrite in composite materials is found. Small peaks are coming near the peak of cobalt ferrite are CCTO peaks. It's due to the composition. Initially there is no additional peak, but as the % of CCTO increases the additional peaks are formed. It confirmed that the prepared composite is crystalline in structure.

4.2 SEM and EDAX Analysis:

The surface morphology of cobalt ferrite and CCTO mixed composites have been studied by scanning electron microscopy method. Fig. 4.2 represents the SEM images of pure $CoFe_2O_4$ and composites of cobalt ferrite. The Composite were prepared by variation of CCTO concentration in cobalt ferrite with the help of chemical route method.
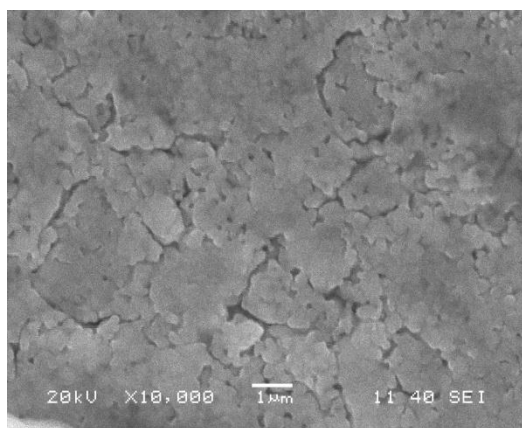
Fig 4.2 (a) pure cobalt ferrite
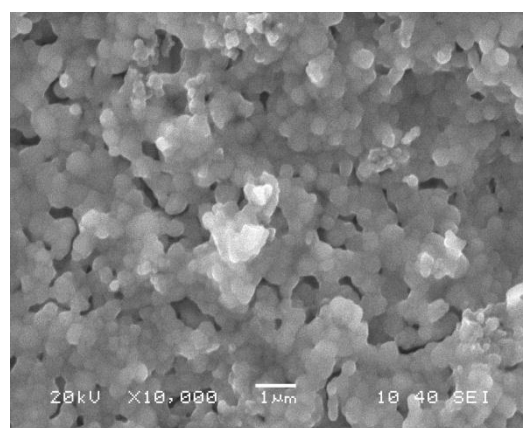
Fig 4.2 (b) $CoFe_2O_4$ and 10% CCTO
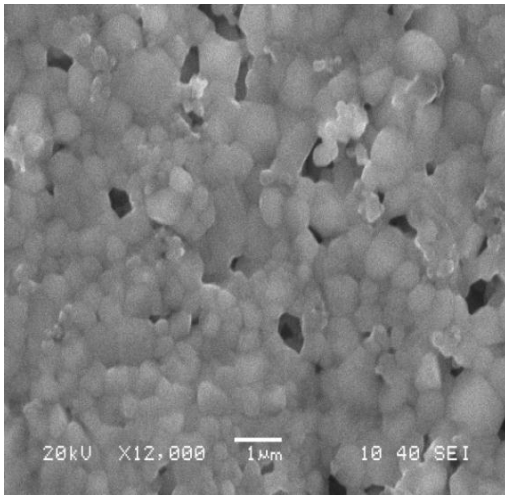
Fig 4.2 (c) CoFe$_2$O$_4$ and 20% CCTO
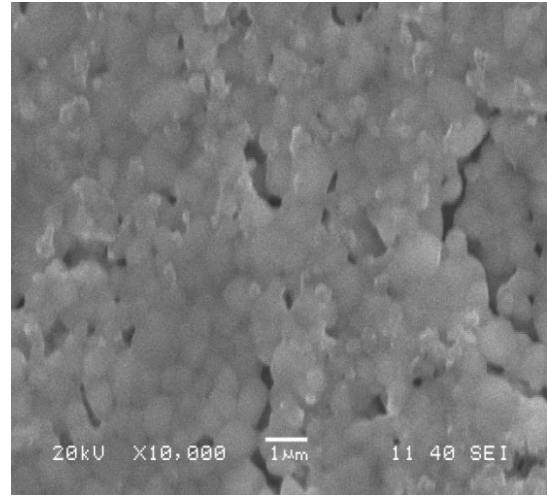
Fig 4.2 (d) CoFe$_2$O$_4$ and 30%CCTO
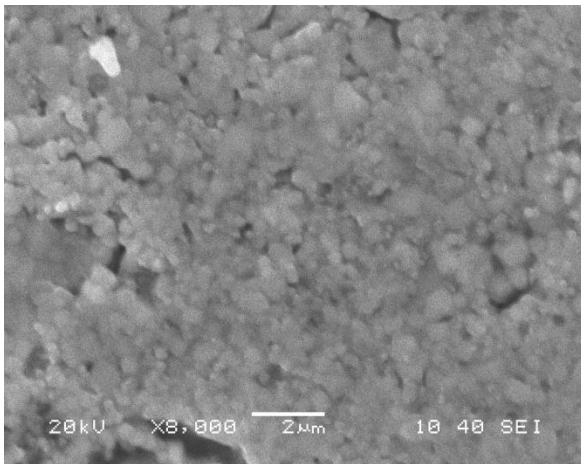
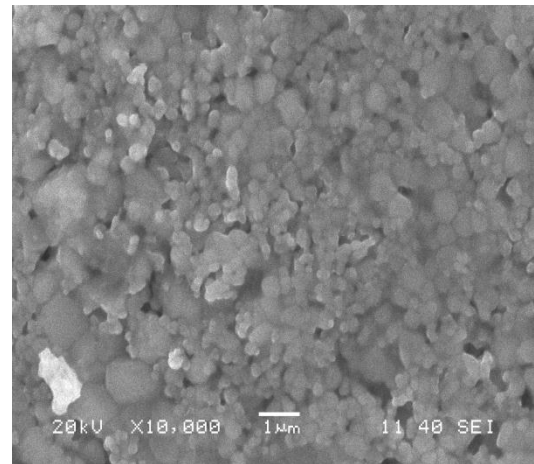Fig 4.2(e) CoFe$_2$O$_4$ and 40% CCTO

Fig 4.2(f) CoFe$_2$O$_4$ and 50%CCTO

From the above pictures we confirm that, as we increases the concentration of CCTO in cobalt ferrite there is no distinct grain boundary. The uniformity decreases. The shapes of the grains are spherical. As the concentration of CCTO increases, the grains are tightly packed, means sizes of grains are reduces.
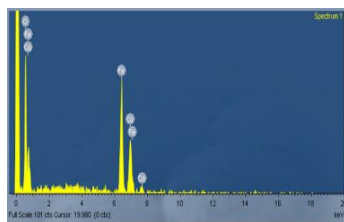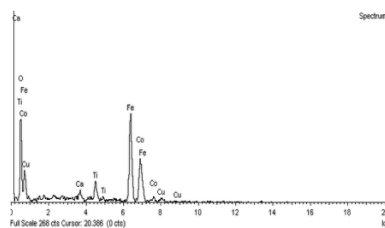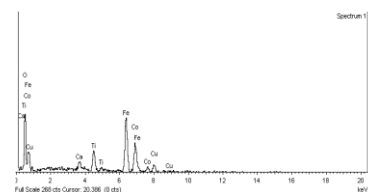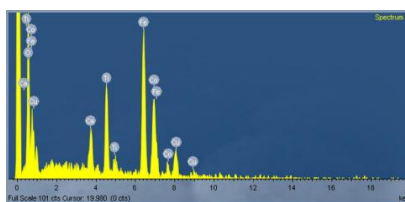
4.3 EDAX Images:

Fig 4.3 (a) pure $CoFe_2O_3$

Fig 4.3 (b) $CoFe_2O_4$ and 10% CCTO

Fig 4.3 (c) $CoFe_2O_4$ and 20% CCTO

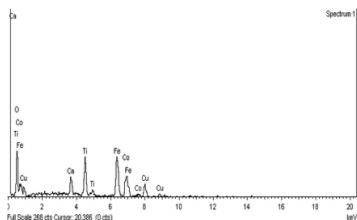Fig 4.3 (d) $CoFe_2O_4$ and 30% CCTO

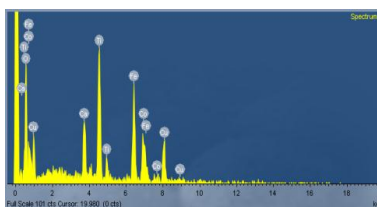Fig 4.3 (e) $CoFe_2O_4$ and 40% CCTO

Fig 4.3 (f) $CoFe_2O_4$ and 50% CCTO

From the above EDAX images, it confirms the percentage of elements presents in that sample. EDAX images generally give the idea about the existence of elements and their percentage.

4.4 Measurement of Dielectric Constant and Dielectric loss:

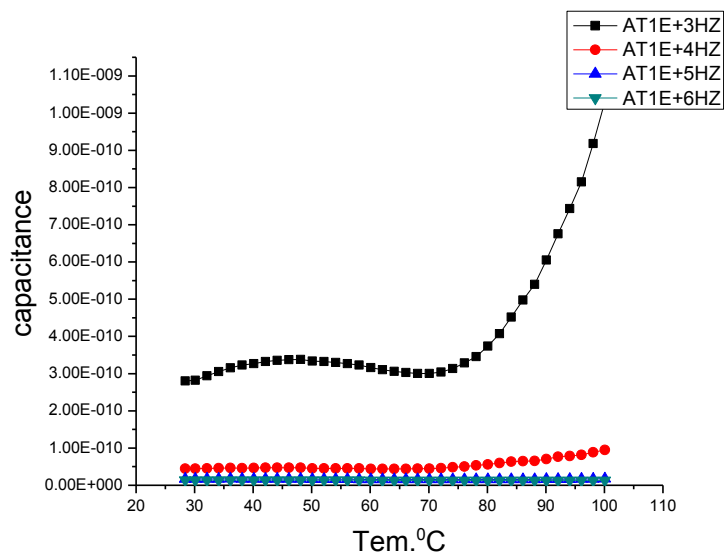## 4.4.1 Dielectric constant:

Fig 4.4.1 (a) Variation of dielectric constant w.r.t temp for 50%
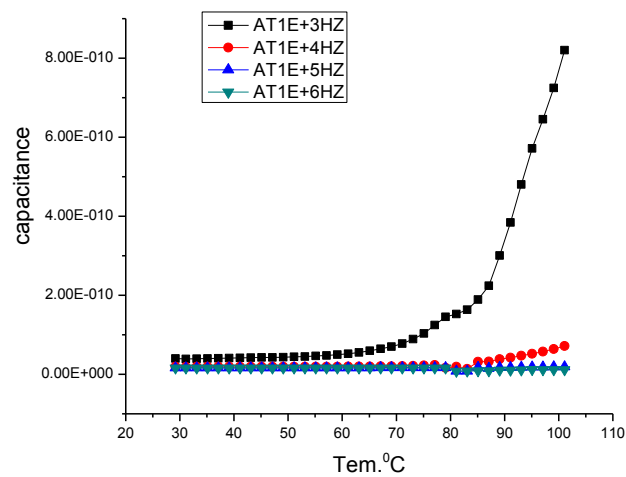

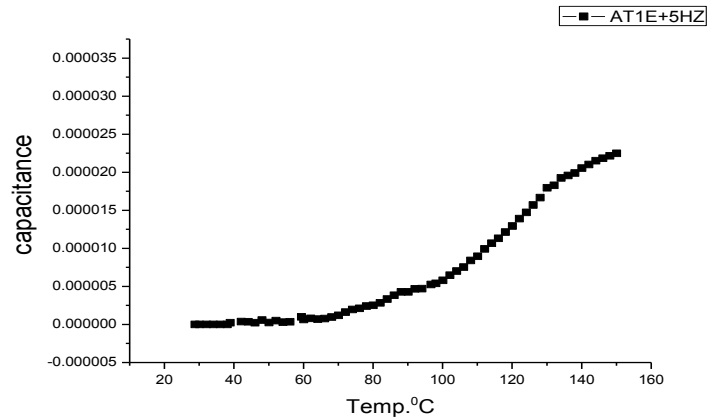Fig 4.4.1 (c) Variation of dielectric constant w.r.t temp for 30%

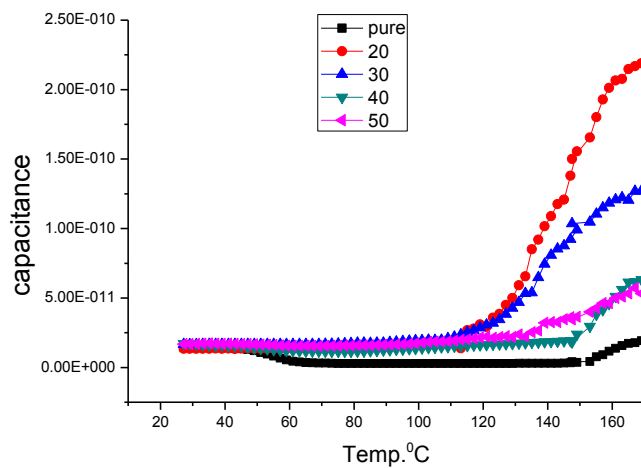Fig 4.4.1 (d) Variation of dielectric constant w.r.t temp for 10%

Fig 4.4.1 (e) Variation of dielectric constant w.r.t temp for different composition at 1000 KHz.

A plateau is observed near room temperature. This is followed by an increase over a rang of temperature. The increase in dielectric constant with temperature due to increase in the space charge. Space charge polarization is present because of chemical microheterogeneities. Microheterogeneities arise due to random occupation of equivalent crystallographic sites. Difference in the chemical composition between these microregions leads to difference between conductivity of these regions. This gives rise to space charge polarization. The conductivity increases exponentially with temperature. Therefore, the difference between conductivity will also increase. This leads to an increase in the dielectric constant at high temperature.

Dielectric constant decreasing with increasing in frequency, as we can see from above graphs at different frequency. But from table 1 and fig 4.4.1(d) dielectric constant is very high in

10% composite. It means more flux density it posses. The value of dielectric constant (ε_r) is found to be decrease with increase in the concentration of CCTO in the composite. This low value can be explained on the basis of the fact that dielectric polarization is reduces.

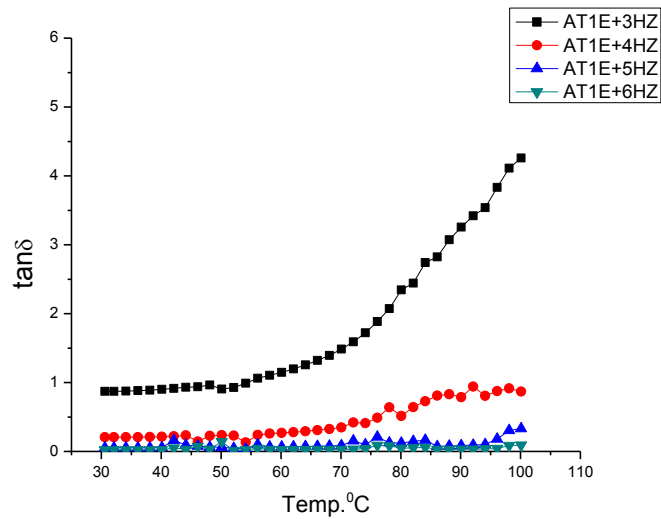### 4.4.2 <u>Dielectric loss:</u>

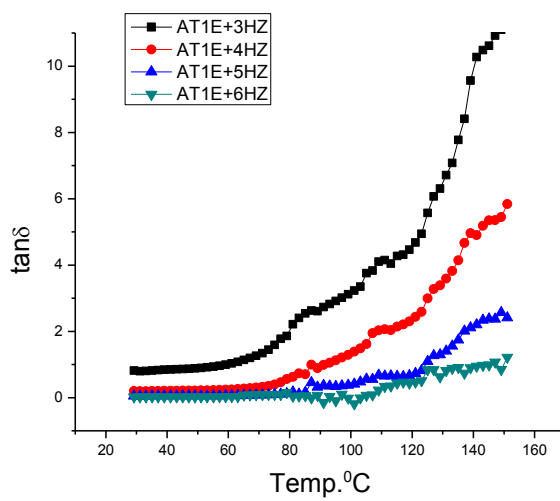Fig 4.4.2 (a) Variation of dielectric loss with respect temperature for 10%.

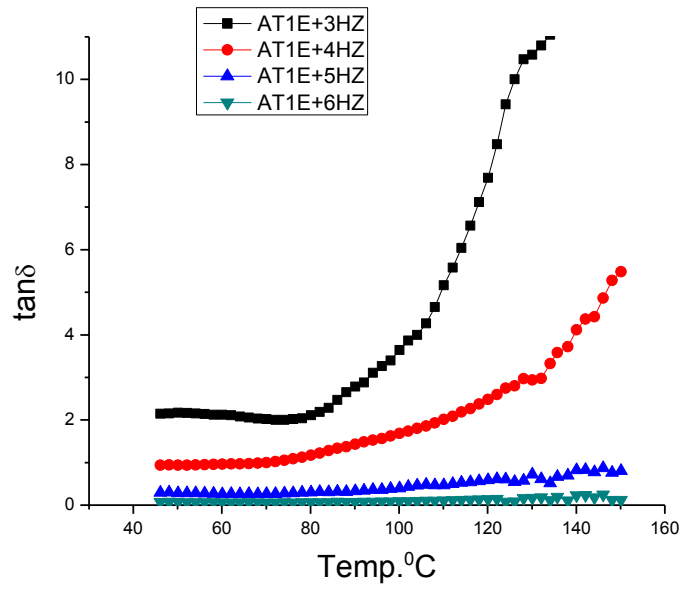Fig 4.4.2 (b) Variation of dielectric loss w.r.t the temperature for 30%.

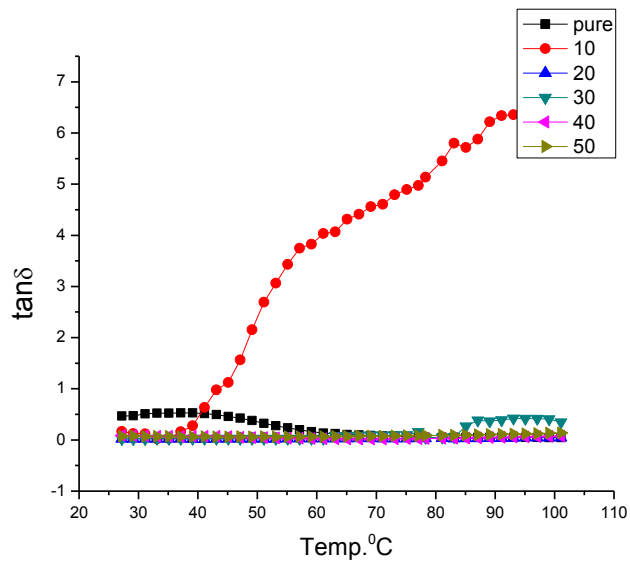Fig 4.4.2 (c) Variation of dielectric loss w.r.t temp for 50%.

Fig 4.4.2 (d) Variation of dielectric loss for 1 MHz

Table 1. Dielectric constant and Dielectric loss at room temperature:

Composition	Dielectric constant (ε_r)	Dielectric loss (tanδ)
Pure cobalt ferrite($CoFe_2O_4$)	2.9×10^7	0.075
$CoFe_2O_4$ + 10% CCTO	8.42×10^7	1.608
$CoFe_2O_4$ + 20% CCTO	5.54×10^7	0.052
$CoFe_2O_4$ + 30% CCTO	3.9×10^7	0.053
$CoFe_2O_4$ + 40% CCTO	3.2×10^7	0.152
$CoFe_2O_4$ + 50% CCTO	3.8×10^7	0.286

Dielectric constant is calculated by:

$$\varepsilon_r = (C \times d) / (\varepsilon_0 \times A)$$

Where ε_r: Dielectric constant

C: Capacitance

d: Thickness of pellet

A: Area of the pellet

ε_0: permittivity of the free space

The variation of dielectric loss (tanδ) with temperature for different composite was shown in above figures. The loss tangent increases with increase in temperature, irrespective of CCTO transition temperature, that ensures the semiconducting nature or thermally activated mechanism of conduction in the composites. Compared Figure 4.4.1 (a) with Figure 4.4.2 (c), the samples show the loss tangent is also increased in proportion to the increase in dielectric constant. All this observation is similar to that reported earlier for the other composite [17]. Crystal structure perfection, porosity, chemical homogeneity and the amount of Fe^{2+} in the sample are effect the dielectric constant and dielectric loss in the cobalt ferrite.

CHAPTER 5

CONCLUSION:

In this study, the cobalt ferrite ($CoFe_2O_4$) is mixed with CCTO (calcium, copper, titanium oxide) and form composites, at different compositions, which sintered at 900^0 C. The sample preparation is made chemical route method. Characterisation was done by XRD and SEM-EDAX of the composites. The presence of uniform sized particles and crystalline in nature has been observed. EDAX analysis suggests the presence of elements such as Co, Fe, O, Cu, Ca and Ti in the mixed composites. From dielectric measurements, the conductivity increases exponentially with temperature. This leads to a rapid increase in the dielectric constant at high temperature. As the percentage of CCTO increase in the composite, the value of dielectric constant (ε_r) increases. The 10 % CCTO composite pellet exhibit high value of the dielectric constant ($\varepsilon_r \sim 8.42 \times 10^7$) as compared to others. Due to this, the 10 % composite can be use for manufacture of high value capacitors. It also has high dielectric loss. The dielectric losses results from the heating effect on the dielectric material.

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