

**STUDIES ON DIELECTRIC AND FERROELECTRIC
PROPERTIES OF CoFe_2O_4 + BNT COMPOSITES**

**Thesis submitted in partial fulfilment of the requirement
for the degree of**

MASTER OF SCIENCE

IN PHYSICS

BY

TAILAKYA NATH GIRI

ROLL-NO-411PH2095

Under guidance of

Dr. D. Behera



Department of Physics

NIT Rourkela, 2012-2013



Dr. Dhruvananda Behera

Associate Professor,

Department of Physics ,

National Institute of Technology,

Rourkela - 769008

CERTIFICATE

This is to certify that the thesis entitled “Synthesis and characterisation of $\text{CoFe}_2\text{O}_4+\text{BNT}$ composite of ferrite” by Tailakya Nath Giri (Roll no-411ph2095) for the partial fulfilment of the requirements for the award of Master degree in physics at National Institute of Technology , Rourkela, is an faithful work carried out by him under my supervision and guidance.

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

Place:

Signature of the guide

Date:

(D. Behera)

ACKNOWLEDGEMENT

We owe our cordial gratitude to our respected teacher and supervisor **Dr D.Behera**, Associate Professor, Department of Physics, National Institute of Technology, Rourkela, whose splendid guidance, authentic supervision, assiduous cooperation, moral support and constant encouragement enabled us to make out our research problem in the present form.

It is our great pleasure to acknowledge to **Dr. Sidhartha S. Jena**, Head of the Physics Department, National Institute of Technology, Rourkela for providing us the necessary facilities for making this research work a success.

We are highly indebted to all our teachers of this department for their kind help and expert suggestions. We express our profound gratitude to **Mr. Ranjit Ku. Panda** (PhD. Scholars) for their ceaseless encouragement, immense help and hearty encouragement during our project work.

We wish to thank all of our friends for making our stay in this institute a memorable experience.

Finally, we must record our special attention to our parents & GOD who has always been a source of our strength, inspiration and our achievements.

(Tailakya Nath Giri)

CANDIATE'S DECLARATION

I hereby declare that the project work entitled “**Synthesis and characterisation of CoFe₂O₄ + BNT composite of ferrite**”, an authentic work is carried by me, during the one year project at NIT, Rourkela, from July 2012 to May 2013 under the supervision of Dr.Dhrubananda Behera and is submitted for the partial fulfilment 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 :

Tailakya Nath Giri

CONTENTS

Chapter 1

1.1	Introduction	(7)
1.1.1	History of CoFe_2O_4	(7)
1.1.2	History of BNT.....	(8)
1.2	Introduction to dielectric and ferroelectric	(11)
1.2.1	Dielectrics	(11)
1.2.2	Polarisation	(11)
1.2.3	Types of polarisation.....	(11)
1.2.4	Frequency dependent dielectric	(12)
1.2.5	Dielectric relaxation.....	(12)
1.2.6	Ferroelectricity.....	(12)
1.2.7	Types of ferroelectricity.....	(13)

Chapter 2

2.0	Experimental details.....	(13)
2.1	Materials required cobalt ferrite.....	(13)
2.2	Synthesis of cobalt ferrite.....	(13)
2.3	Material required for BNT.....	(13)
2.4	Synthesis of BNT.....	(13)
2.5	Composite formation.....	(14)
2.6	Characterisation techniques.....	(14)
2.6.1	X-ray diffraction	(14)
2.6.2	Scanning electron microscope(SEM).....	(15)
2.6.3	P-E loop study.....	(17)
2.6.4	Dielectric measurement.....	(18)
2.6.4.1	Dielectric constant measurement.....	(18)
2.6.4.2	Tangent loss.....	(18)
2.6.5	conclusion	(20)

ABSTRACT

Now a days the materials which are showing both ferroelectric and ferromagnetic properties are interesting. In this work, we have prepared cobalt ferrite and bismuth sodium titanate composites by conventional ceramic method. With X-ray Diffraction the phase is confirmed with no other impurity peaks. By the help of SEM the surface morphology of composite is characterisation. From ferroelectric study, it is observed that the coercivity decreasing and remnant polarisation, saturation polarisation are increasing with BNT weight fraction. Variation of dielectric constant with respect to the frequency has been studied. It is observed that dielectric constant is decreasing with frequency and increasing with increasing weight fraction of BNT.

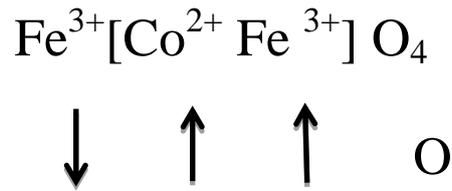
INTRODUCTION

Last few years scientist are showing interest on the materials exhibiting both ferromagnetism and Ferro electricity known as multiferroics. Multiferroic materials have applications in transducers, actuators, capacitors and memory applications [1]. Multiferroic term was first used by H. Schmid in 1994 [2]. Multiferroics are originally defined as a single phase materials have the at least two properties among the four. They are Ferro electricity (possess stable and spontaneous polarisation), ferromagnetism (possess spontaneous deformation), ferroelastic and Ferrotoroidic (which possess stable and spontaneous order parameter) properties. Now days most researchers are showing interest on the multiferroic composites like cobalt ferrite/barium titanate composites, cobalt ferrite/barium strontium titanate composites, $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4/\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$, $\text{NiFe}_2\text{O}_4/\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ [3] i.e the combination of spinel ferrites with ferroelectric materials showing interest. In this present work, we have studied the ferroelectric and dielectric properties of the cobalt ferrite and bismuth sodium titanate composites.

Cobalt ferrite:

Cobalt ferrite belongs to $Fd\bar{3}m$ space group and lattice parameter typically ~ 8.4 Å. We know that in cobalt ferrite oxygen forms cubic structure so that there will be 64 tetrahedral sites and 32 octahedral sites. Each unit cell contains 8 chemical formulas so that eight ferric ions occupy tetrahedral sites and eight cobalt ions and eight iron ions occupy octahedral ions [4].

Magnetically cobalt ferrite is ferromagnetic material. The magnetic moments of the cations in the tetrahedral site are parallel and in the same way, spins of the cations in the octahedral sites are parallel. But the spin arrangement between tetrahedral and octahedral site is anti-parallel. In cobalt ferrite, spins of eight ferric ions in tetrahedral site cancel with the spins of the eight ferric ions in the so the resultant magnetic moment comes from the cobalt ion when it is completely inverse. Resultant magnetic moment depends on inversebility also. Spin alignment of cobalt ferrite is shown below when it is inverse spinel. The square bracket represents



Octahedral Site [5,6]. Therefore, the resultant spin comes from the cobalt ion which is equal to $3\mu_B$ per molecule when it is completely inverse structure. Generally, eighty percent of the cobalt will be in the octahedral site. If x is the inversion factor then calculated net spin will be $7-4x$ for molecule of cobalt ferrite.

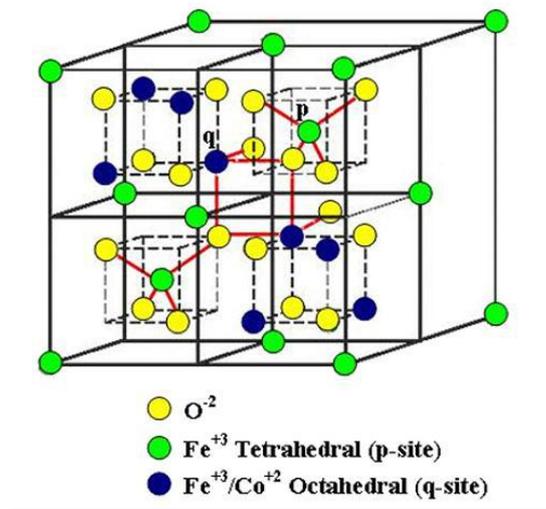


Fig.1. Cobalt ferrite unit cell

Bismuth sodium titanate:

Bismuth sodium titanate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$) or BNT is known to be one of the promising candidates for lead free materials. It is ferroelectric at room temperature, having the perovskite structure with a formula ABO_3 where Bi and Na situate at A site. It also has a rhombohedral crystal structure. Bismuth sodium titanate is an ABO_3 distorted perovskite with an rhombohedral $R3c$ crystal structure at room temperature. The standard ABO_3 perovskite formula for BNT is $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ [7]. An ABO_3 perovskite can be considered in two ways;

one way is to have the bismuth and sodium cations occupy the corners of a cubic unit cell, oxygen cations occupying the face centers, and a titanium cation in the center of the oxygen Octahedra that is formed. The other way, is a three-dimensional cubic network of 8 corner-sharing TiO_6 octahedra with bismuth and sodium cations at the center of the cube formed by the octahedra. Figure 1 represents a typical ABO_3 perovskite, shown here as cubic BNT. The figure suggests that the bismuth and sodium ions are ordered on the A site of the structure; this is only to show the stoichiometry that is present in an ideal mixture. The real material does not exhibit any long range ordering as described later. The BNT compound has an anomaly phase transformation of ferroelectric rhombohedral to ant ferroelectric tetragonal at about $220^{\circ}C$ and to Para electric tetragonal phase at $T_c = 320^{\circ}C$. The tetragonal phase above $320^{\circ}C$ finally changes to cubic phase above $520^{\circ}C$. At $320^{\circ}C$, the dielectric constant is highest and temperature dependence of the BNT ceramics shows a diffused behaviour with strong ferroelectricity similar to relaxor-type ferroelectrics. The bismuth sodium titanate (BNT) family of dielectric materials is a relatively new family of dielectrics [8,9]. It is being studied because of its high temperature dielectric constant, as well as its ability to work well without the addition of lead. BNT is a candidate material for future dielectric and piezoelectric applications that cover large temperature ranges. The large temperature range is advantageous for use in the oil and natural gas industry for down-hole drilling tools, automotive, aerospace and military for applications directly on or near hot engine surfaces. BNT is being studied to create a material that could someday replace the current industry standard, barium titanate.

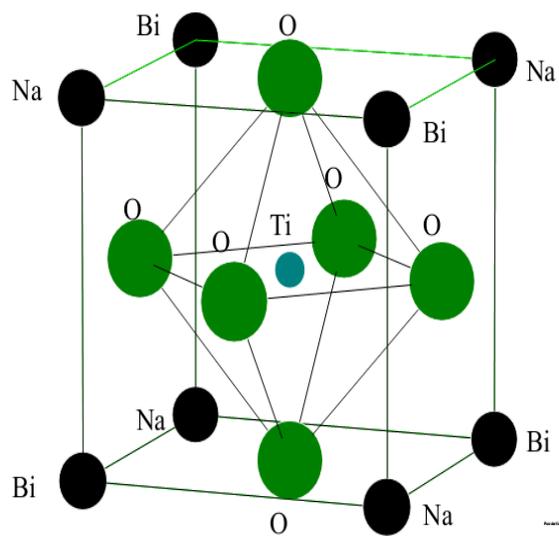


Fig.2. Unit cell of Bismuth sodium titanate

The rhombohedral R3c space group is polar with parallel cation displacements along the $[111]_p$ pseudocubic direction along with antiphase a-a-a- oxygen octahedral rotations. Thorough explanations of the types of octahedral tilting and the associated mechanisms are available to more fully understand this phenomenon (Woodward1997). Cation displacements along with octahedral rotations allow the crystal to have a spontaneous polarization (P_s); polarization is necessary for a material to be ferroelectrically active. The tetragonal P4bm phase is also a polar phase, although it has a weaker polarization response than the R3c phase. The oxygen octahedra in the tetragonal phase exhibits a₀a₀a- rotation behaviour about the c axis with anti-parallel cation displacements of A-site cations along the polar c-axis. The tetragonal phase distortion produces a weaker polarization response because the atomic displacements are less than those in the R3c phase. Smaller atomic displacements result in a lower polarization in the material. This is evident by the decrease in relative permittivity above the Curie temperature (320°C) [10,12].

Temperature(°C)	Phase(s)	Lattice parameters (angstroms)	Glazers tilt system
-260 to 255	Rhombohedral-R3c	$a_H=5.4887(2)$ $c_H=13.5048$	$a^- a^- a^-$
255 to 400	Coexisting Rhombohedral/tetragonal	variable	mixture
400 to 500	Tetragonal – P4bm	$a_T= 5.5179 (2)$ $c_T= 3.9073$	$a^0 a^0 a^-$
500 to 540	Coexisting Tetragonal/Cubic	Variable	Mixture
Above 540	Cubic Prototype – Pm3m	$a_C = 3.91368 (3)$	None

Introduction to Dielectrics and Ferroelectrics:

The recent advances in ceramic technology have brought about a revolution in the digital world. Research in the field of dielectrics is leading to newer inventions each day. However, to understand the hidden capacities of a dielectric material, the first thing that comes to one's mind is what a dielectric exactly is. A brief introduction to the theory of ferroelectrics as well as dielectrics is addressed in the sections that follow.

Dielectrics:

Dielectrics are mainly insulators that can be polarized by the application of electric field. When a dielectric material is placed in an electric field, electric charges do not flow through it (like in conductors) but shift from their average equilibrium positions causing polarization. The amount of polarization caused is described by a dimensionless quantity called the dielectric constant.

Polarization:- On placing in an electric field, the positive and negative charges of a dielectric are displaced from their equilibrium positions by very small distances throughout the volume of the dielectric. This results in the formation of a large number of dipoles each having some dipole moment in the direction of the field. The material is said to be polarized with a polarization P . The polarization is defined as dipole moment per unit volume.

Types of polarization:

1. **Electronic polarization:** This type of polarization arises due to the displacement of the electron cloud of an atom relative to its nucleus in the presence of an applied electric field. The polarization as well as the dielectric constant of a material at optical frequencies results mainly from electronic polarization.
2. **Ionic polarization:** Ionic polarization arises due to displacement of a charged ion relative to other ions in a solid. The ionic contribution is important at low frequencies.
3. **Dipolar polarization:** The dipolar polarization arises due to polar substances that can orient themselves in the presence of an external electric field. The thermal agitation of the molecules tends to counteract the ordering effect of the electric field and an equilibrium state

is reached wherein the different dipoles make all possible angles varying from zero to π radians with the field direction.

4. Space charge polarization: Space charge polarization arises due to the accumulation of charges at the interface or at the grain boundary of a polycrystalline material. The ions diffuse over appreciable distances in response to the applied field-giving rise to re-distribution of charges in the dielectric medium [11].

Frequency dependence of dielectrics:

Dielectric constant, or, of a dielectric material decreases with increase in frequency. The dielectric loss at low frequencies is mainly due to d.c. resistivity.

However, at high frequencies the dielectric loss is mostly due to dipole rotations or due to ionic transitions from the lower energy states to higher energy states. Because of the upward transition, the energy is absorbed from the applied field. The absorption of energy is possible if orientational polarization or permanent dipole moments are present.

Dielectric relaxation:

Dielectrics take a finite time for the polarization to reach its maximum value. This is due to the forces between adjacent molecules, which tend to prevent the alignment along the external field. This phenomenon is called dielectric relaxation. It is an inherent property of relaxor ferroelectrics [12].

Ferroelectricity :

Types of ferroelectrics

Ferroelectric crystals can be classified under two types of transitions – displacive or order disorder.

1. **Displacive:** If propagation of soft phonon mode is allowed in the crystal at transition, then the transition is displacive.

2. **Order-disorder:** If the soft mode is diffusive but not propagating, the phonon does not exist but allows a large amplitude hopping motion between the wells of the order-disorder system. They can also be classified as normal or relaxor ferroelectrics on the basis of frequency dependence of ϵ_r .

a. **Normal ferroelectrics:** Normal ferroelectrics show either first or Second order phase transition at Curie point T_C . They show weak frequency dependence and follow Curie-Weiss law. They show a large remnant polarization as compared to relaxor ferroelectrics. Normal ferroelectrics do not show any hysteresis loop about T_c .

b. **Relaxor ferroelectrics:** Relaxor ferroelectrics show a broad diffuse Phase transition at Curie maxima. They also show strong frequency dependence and follow Curie-Weiss square law. They show a weak remnant polarization as compared to normal ferroelectrics. Relaxor ferroelectrics show a hysteresis loop about T_C [13].

Synthesis of cobalt ferrite and bismuth sodium titanate

Composites:

Cobalt ferrite, BNT were prepared separately by conventional solid state method.

Preparation of Cobalt ferrite:

Co_3O_4 , Fe_2O_3 have taken as precursor materials for the synthesis of cobalt ferrite. These oxides were mixed in required ratio and grinded for one hour resulting brown powder. The mixed powder was calcined at 900°C for 7 hours with heating rate 5°C per minute and cooled to the room temperature at the same cooling rate. Finally a black coloured cobalt ferrite powder was formed.

Preparation of BNT:

Bi_2O_3 , Na_2CO_3 and TiO_2 used as raw materials for the preparation of Bismuth sodium titanate. These raw materials were mixed in required ratio and grinded for one hour. After that mixed powder was calcined at 850°C for 3 hours with heating rate 5°C per minute and cooled to room temperature with same cooling rate to get the BNT powder.

Composite preparation:

CFO and BNT composites are prepared by mixing the 10, 20, 30, 40 % weight percentages of BNT with the cobalt ferrite as a major material and grinded for 2 hours with the help of binder. After that they are palletised and sintered at 1000° C for two hours.

CHARACTERIZATION:

Characterization Techniques:

All the samples were characterised by various techniques such as X-Ray diffraction (XRD), Scanning electron Microscope (SEM) and dielectric measurement. X-ray diffraction pattern were recorded on a PAN analytical diffractometer (PAN-PW 1830) using Ni filtered Cu K α ($\lambda = 1.541\text{\AA}$) radiation within the 2θ range from 20 to 80 at a rate of 20 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

X-ray diffraction:

In nanoparticle study, X- ray diffraction patterns have been broadly 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.

Scanning electron microscope (SEM):

A SEM can be used for high magnification imaging of almost all materials. The surface morphology of the sample was studied using JEOL JSM-5300 microscope (acceleration voltage 15 KV). On a carbon tape the sample powder were deposited previously 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.

XRD diffractogram

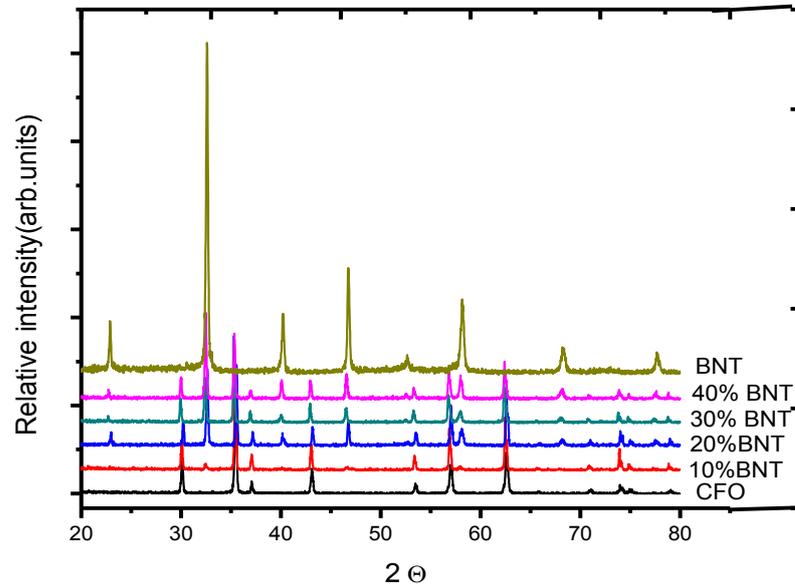


Fig.3 XRD pattern of the cobalt ferrite and bismuth sodium titanate composites.

XRD ANALYSIS:

Fig shows the XRD spectra of the CFO/BNT composites. XRD analysis of sintered ceramic samples showing two phase composition of constituent phases. No other phases are identified so that no chemical reaction at ferromagnetic and ferroelectric interface. The peaks are indexed as cubic spinel ferrite and Rhombohedral perovskite ferroelectric phases.

SEM image

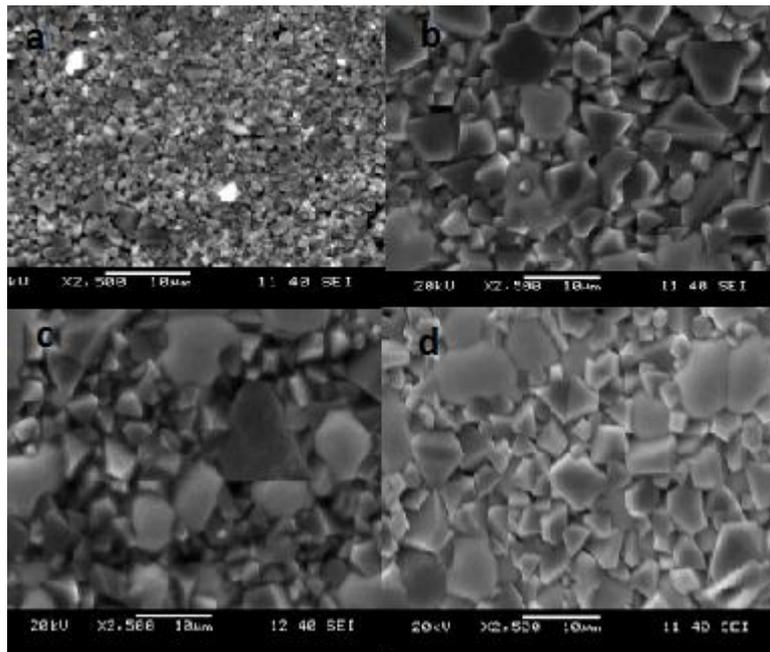


Fig.4 SEM image of the cobalt ferrite and bismuth sodium titanate composites.

SEM ANALYSIS:

The backscattered SEM graphs of the composites ($x = 0, 20, 30, 40$) are shown in Figure. It can be shown that the composites are dense, have fewer pores, and no cracks. As we increase the concentration of BNT in cobalt ferrite there is no distinct grain boundary. The uniformity decreases. As the concentration of BNT increases sizes of grains are increases.

FERROELECTRIC PROPERTIES

Fig. 5 shows P-E loops of the CFO+BNT composites and these loops are indicating that composites are ferroelectric characteristics.

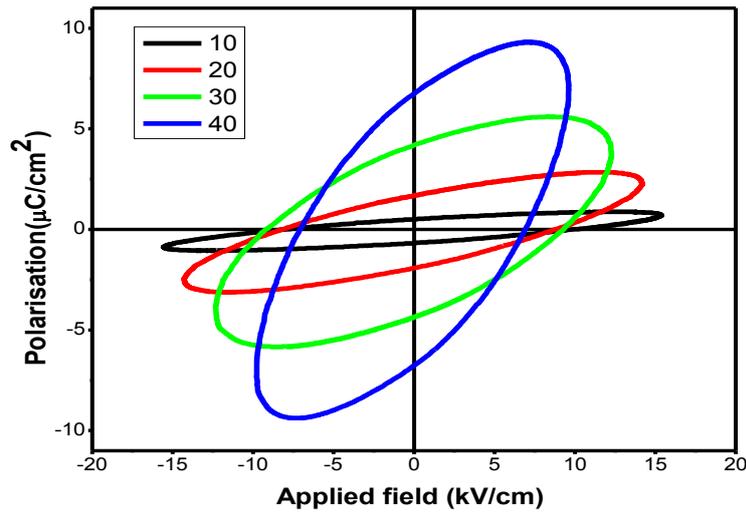
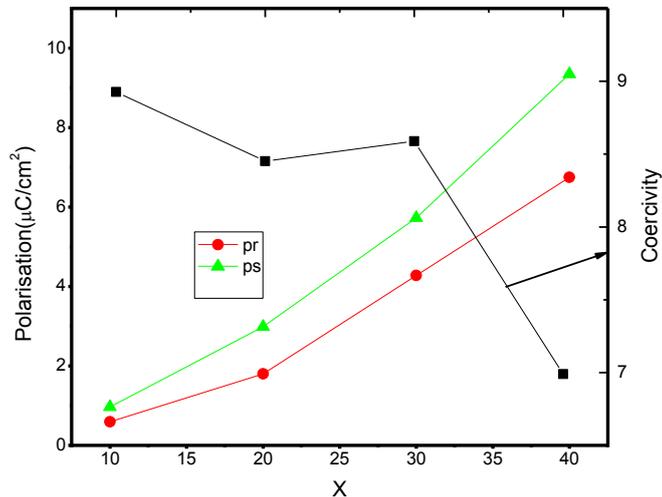


Fig.5. P E loop of the cobalt ferrite and bismuth sodium titanate composites.



The remanent polarisation and saturation polarisation are increasing with increasing percentage of BNT because it increases the ferroelectric nature. But coercivity is decreasing with increasing percentage of BNT that is due to the hindering and pinned domain wall motion of ferroelectric regions due to the existence of ferrite phase [14].

DIELECTRIC PROPERTIES:

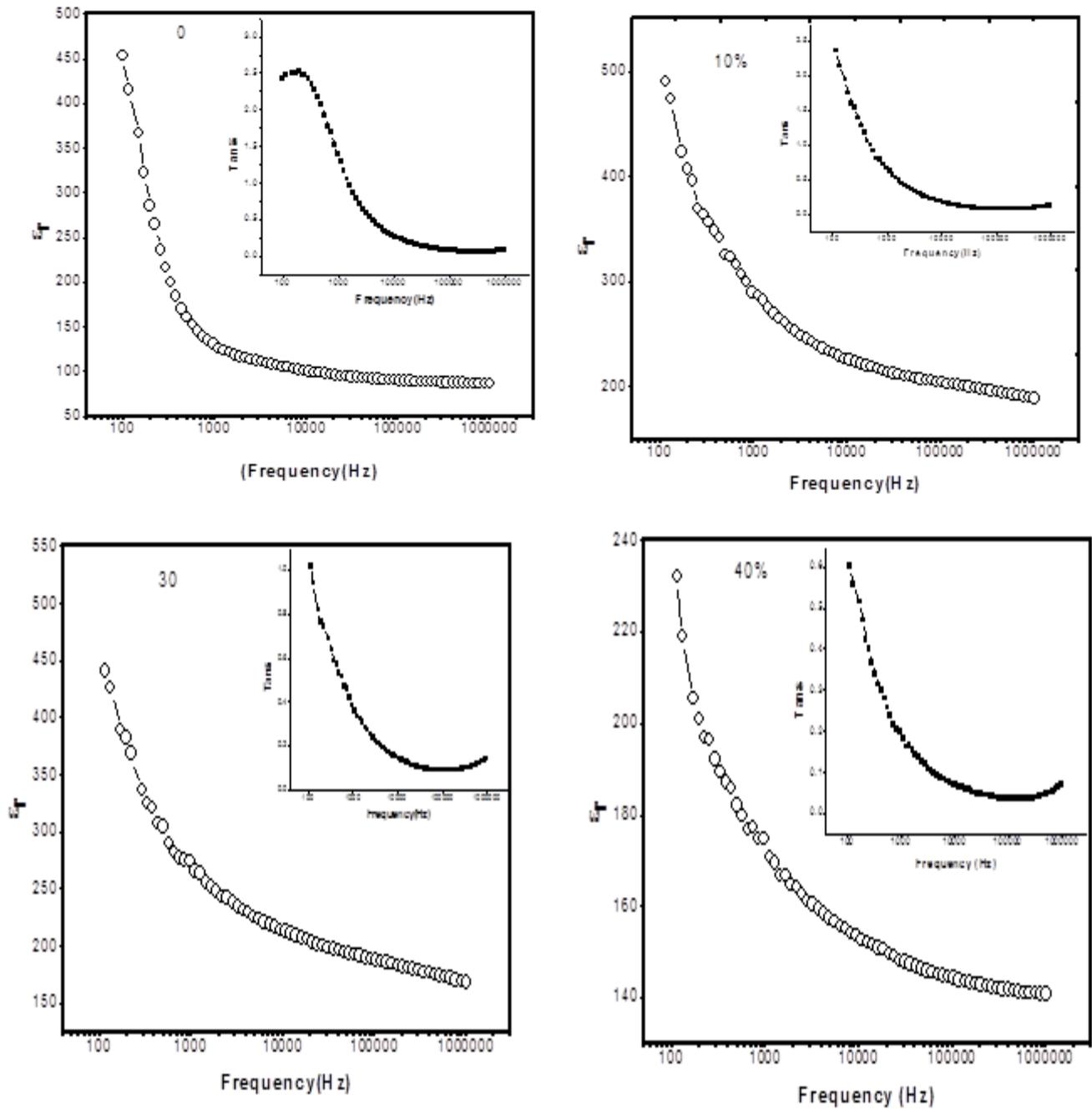


Fig.6 Variation of Dielectric constant with frequency at room temperature.

The Variation of the dielectric constant with frequency at room temperature for different CFO+BNT composites as shown in figure-4. From the figure it is noticed that the dielectric constant is decreasing with increasing frequency which is typical dielectric behaviour of spinel ferrites. The larger value of dielectric constant at lower frequencies is due to the all contribution (atomic, electronic, ionic and interfacial polarisation). As frequency increases the contribution from the space charge and orientational polarisation reduces so dielectric constant decreases. At higher frequency the dielectric constant completely ceases.

S.No	composition	Dielectric constant		
		1KHz	10KHz	100KHz
1	CFO	130	101	90
2	10%	289	225	204
3	30%	274	214	188
4	40%	174	152	144

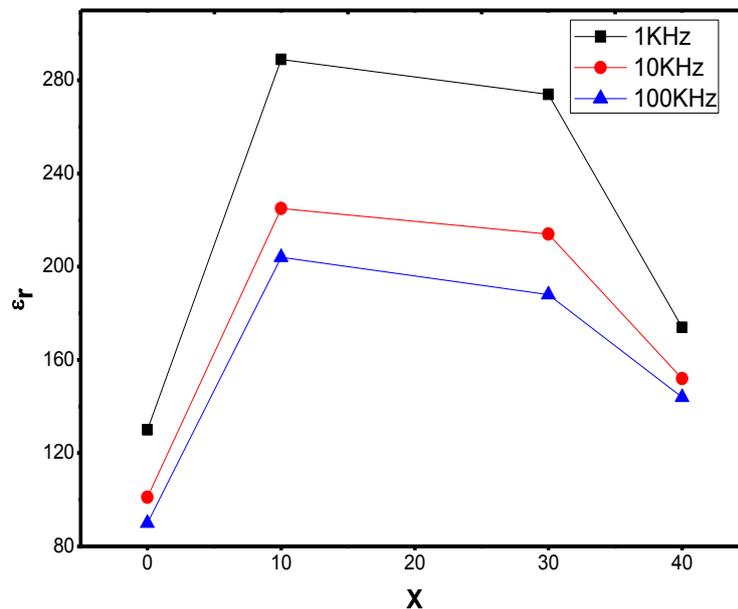


Fig.7 variation of the dielectric constant with respect to the BNT percentage

Dielectric constant is increased after the addition of BNT to the cobalt ferrite. Addition of 10% of BNT to the cfo is showing high dielectric constant than other compositions. 30% and

40 % of BNT addition are showing lower dielectric constant compare to the 10% BNT addition but higher dielectric constant than the parent.

CONCLUSSIONS:

- 1) CFO/BNT composites are prepared by the conventional ceramic method.
- 2) XRD analysis conformed that there is no chemical interaction between ferroelectric and ferromagnetic phases in the composites.
- 3) SEM figures are showing that the composites are dense, have fewer pores, and no cracks.
- 4) The coercivity is decreasing; remnant polarisation and saturation polarisation are increasing with the BNT weight fraction.
- 5) Dielectric constant is decreasing with increasing frequency and increasing with weight percentage of BNT.

References:

- 1) Yun Zhou et al., Journal of Alloys and Compounds 484 (2009) 535–539
2. H. Schmid. Ferroelectrics 162, 317 (1994).
- 3) D.R. Patil, B.K. Chougule, J. Alloys Compd. 458 (2008) 335–339.
- 4) Mohd. Hashim, Alimuddin , Journal of Alloys and Compounds 518, 11–18 (2012).
- 5) Atsuto Seko, Fumiyasu Oba, and Isao Tanaka, Physical review B 81, 054114(2010).
- 6) T.A.S. Ferreira, J.C. Waerenborgh, M.H.R.M. Mendonça , M.R.Nunes and F.M.Costa, Solid State Sciences 5, 383–392 (2003)
- 7) Simona Burianova, Jana PoltieroVa Vejpravova, Petr Holec, Jiri Plocek and Daniel Niznansky, Journal of Applied Physics 110, 073902 (2011).
- 8) A. Franco, Jr.,F. L. A. Machado and V. S. Zapf, Journal of applied physics 110, 053913 (2011).
- 9) Ibrahim Sharifi, H.Shokrollahi, MohammadMahdiDoroodmand and R.Safi, Journal of Magnetism and Magnetic Materials 324, 1854–1861 (2012).
- 10) H. S. Mund, Shailja Tiwari, Jagrati Sahariya, M. Itou, Y. Sakurai and B. L. Ahuja, Journal of Applied Physics 110, 073914 (2011)
- 11) R. Valenzuta, magnetic ceramics, Cambridge university press, New York (1994).
- 12) Bond valence structure analysis of doped Bismuth Sodium Titanate by Conor James Walsh, Alfred University ,New York,2004.
- 13) Ahmad Safari, Rajesh K.Panda, and Victor F.Janas *Ferroelectric Ceramics:Processing, properties and applications*
- 14) Yean Wang et.al.,journal of material science: Mater Electron(2012) 23:1064-1071