MULTIFERROIC COMPOSITES
AN OVERVIEW

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of technology
In
Ceramic Engineering

By

BINIT KUMAR

Department of Ceramic Engineering
National Institute Of Technology
Rourkela
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Under the guidance of
Prof. J.bera

Department Of Ceramic Engineering
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Rourkela

CERTIFICATE

This is to certify that the thesis entitled "----------
----------" submitted by Sri/Ms----------in partial fulfillment of the requirements for the award of Master of Technology/Bachelor of Technology degree in ---------- Engineering with specialization in"----------
----------" at the National Institute Of Technology Rourkela (Deemed university) is an authentic work carried out by him /her under my /our supervision and guidance.

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

DATE……..

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BINIT KUMAR

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ABSTRACT

Multiferroics, i.e. materials with magnetic and electric order coexisting, have been attracting much of interest the latest years. The interaction of magnetic and electric subsystems manifests itself as magnetoelectric (ME) effect that is interesting for practical applications such as the sensor techniques, microelectronics and magnetic memory systems.One of the most attractive substances for creation of new ME materials is the bismuth ferrite BiFeO3 .due to its record high temperatures of electric (Tc ¼ 1083 K) and magnetic (TN ¼ 643 K) ordering. Noteworthy that the Giant ME effect at room temperature has been obtained for the first time in thin films of this material . In the bulk BiFeO3 samples the spatially modulated spin structure exists in which the magnetization vectors of antiferromagnetic sublattices change periodically from point to point with a period 620A ˚ , incommensurate to the crystal lattice period (spin cycloid). The presence of spatially modulated spin structure results in zero value of the volume-averaged ME effect. A necessary condition for ME effect observation is the suppression of spin-modulated structure, that takes place in strong magnetic fields when the system undergoes the incommensurate–commensurate (IC–C) phase transition between spin-modulated and homogenous antiferromagnetic states. It has been noted in Ref. that there is a profound analogy between spatially modulated spin structures in multiferroics and spatially modulated structures in

nematic liquid crystal (director vector waves). This periodic director vector structures in nematic liquid crystal arise in external electric field (flexoelectric effect) and can be controlled with the electric field. The question arises whether the electric field can control spatially modulated structures in multiferroics in the same way as in liquid crystal

CHAPTER-1

CHAPTER OBJECTIVE

AN INTRODUCTION TO MULTIFERROIC COMPOSITES

1. MULTIFERROIC COMPOSITES—AN INTRODUCTION

The materials which posses two or more types of orders simultaneously, envisioned in a wide range of applications, including electrically controlled microwave phase shifters or ferromagnetic resonance devices,magnetically controlled electro-optic or piezoelectric devices, broadband magnetic field sensors and ME (MAGNETO-ELECTRIC) memory devices are called multiferroic composites for example nickel zinc ferrite, lead zirconate titanate barium strontium titanate(BSTO)-barium hexaferrite(BaM) like etc..In multiferroic materials at least two ferro-type order parameters corresponding to different microscopic degrees of freedom coexist simultaneously such a scenario can combine e.g. ferro-orbital order ,Ferroelasticity ,ferromagnetism or ferroelectricity while coexistence of ferroelectricity and ferromagnetism is rarely found . The possible coupling of both sectors, i.e. the strong variation of electric(magnetic) properties under application of a magnetic(electric) field, which is found in some of these materials, makes them highly attractive for potential applications in micro-electronics. At room temperature , CdCr2S4 multiferroic is a cubic spinel . The Cd2+ ions on the structural A-sites carry a magnetic orbital degree of freedom.The Cr3+ ions on the octahedrally surrounded B-sites possess half filled t2g shells and thus are orbitally inactive. Ferroelectric- ferrite composites ceramics can provide both inductance and capacitance so these materials can be used to design and produce passive EMI filters integrating inductive and capacitive elements .these components have intensive industrial requirements for suppressing electromagnetic/radio frequency interference in electronic circuitry .PZT(ferrite-lead zirconate titanate) in this composite ME coupling is mediated by mechanical stress because of magneto-striction dynamic deformation is produced in ferrites by the applied magnetic field. The reason behind it low resistivity of ferrites (i) that limits the electric field for poling ,leading to poor piezoelectric coupling and (ii) generates leakage current through the sample that results in loss of charges generated piezoelectrically .while these problems can easily be eliminated in layered structures .A 40 fold increase in the strength of magnetoelectric(ME) is reported in layered samples of NFO(nickel ferrite) lead zirconate titanate (PZT) compare to bulk samples .the traverse and longitudinal couplings

are of equal magnitude .The ME coupling strengthens by an order of magnitude when high resistivity modified NFO is used in the composites .A further enhancement of ME interactions is accomplished in bilayer and multilayer structures .the coupling is dependent on the Zn substitution. Bulk samples of pure NFO and PZT prepared either by traditional ceramic processing or by microwave sintering show very weak coupling .An order of magnitude improvement in ME coupling is observed with the use of modified NFO .While the modification involved non-stoichiometric-fe-deficient NFO with a small addition of Co to eliminate the potential formation of divalent Fe ,there by obtaining high resistivity .further enhancement in ME coupling ,by a factor of 5, is observed in layered structures of thick films of NFO and PZT .Substitution of Zn in NFO is observed to influence the strength of pseudo-piezoelectric and ME couplings in multilayers .the ME voltage coefficient is maximum for 20% Zn .Materials exhibiting simultaneous ferroelectricity and magnetism are known as ferromagnets(FEM), which are a class of multiferroic.because of existence of the two or three formalisms these materials have wide range of applications like sensors, phase shifters ,amplitude modulators and optical wave devices .the ME effect is defined as the dielectric polarization of a material in an applied magnetic field or an induced magnetization in an external electric field ,this effect would make the conversion between electric energy and magnetic energy possible which provides opportunities for potential applications as ME memories ,waveguides ,transducers and actuators. The ME effect was first experimentally observed by Astrov in 1960 in Cr_2O_3 and lots of monophase materials had been widely investigated during past few decades Due to the low Neel or Curie temperature and weak ME effects .When a magnetic field is applied to the composites ,the magnetostrictive phase changes its shape firstly and the induced strain is passed to the piezoelectric phase , resulting in an electric polarization .The ME voltage coefficient in these multiphase composites ,especially in laminate structures has been found two or three orders in magnitude stronger than that in single phase ones ,which could be better applied to commercial devices ,leaving alone the intrinsic limitation in the feature size and miniaturizing difficulties of the layered structures ,it is still hard .Relaxor ferroelectrics are also known to have very very large electrostrictive responses. ZnO varistors are semi conducting ceramics having highly non-ohmic current-voltage characteristics which are fabricated by sintering of ZnO powders with small amounts of additives such as Bi_2O_3,CoO,MnO and Sb_2O_3.The non-ohmic property comes from grain boundaries between semiconducting ZnO grains.Due to their superior electrical properties , these materials have become important as varistor

materials for voltage surge protectors in electrical circuits. Varistors provide bidirectional transient protection and very effective in suppressing high amplitude and low frequency transients. Ferrite components can be used as the inductor component and varistors as the capacitor component,to equip the electronics industry with high performance,cost effective filters to control troublesome EMI. Ni-Zn ferrites are soft ferrimagnetics ceramic materials and are commonly the ferrites of choice for EMI applications having very high resistivity .To reduce unwanted crystallite coarsening and particles aggregation, attempts have been made to synthesize nano composites by embedding nanoparticles in a suitable matrix such as silica . Encapsulating magnetic nanoparticles in silica is promising and important approach in the development of magnetic nanoparticles in the technological and biomedical applications. Also it may help to understand the magnetic behavior of nano particles due to new possible surface, interparticles , and exchange interactions in magnetic/nonmagnetic matrix.

Various methods including sol-gel, aerosol, pyrolysis and stober process have been developed to coat magnetic nanoparticles with silica.

Recently, the fabrication of magnetic particle-silica core-shell nanocomposites has been reported using microemulsion route. The water in oil (w/o) microemulsion can provide a unique environment to synthesize novel magnetic nano composites. Nano crystals of NiZn ferrite in the matrix of nanosized silica particles using two step microemulsion process . The nano composites have a novel structure like water melon seeds (NiZn ferrite nanoparticles) being uniformaly dispersed in the flesh

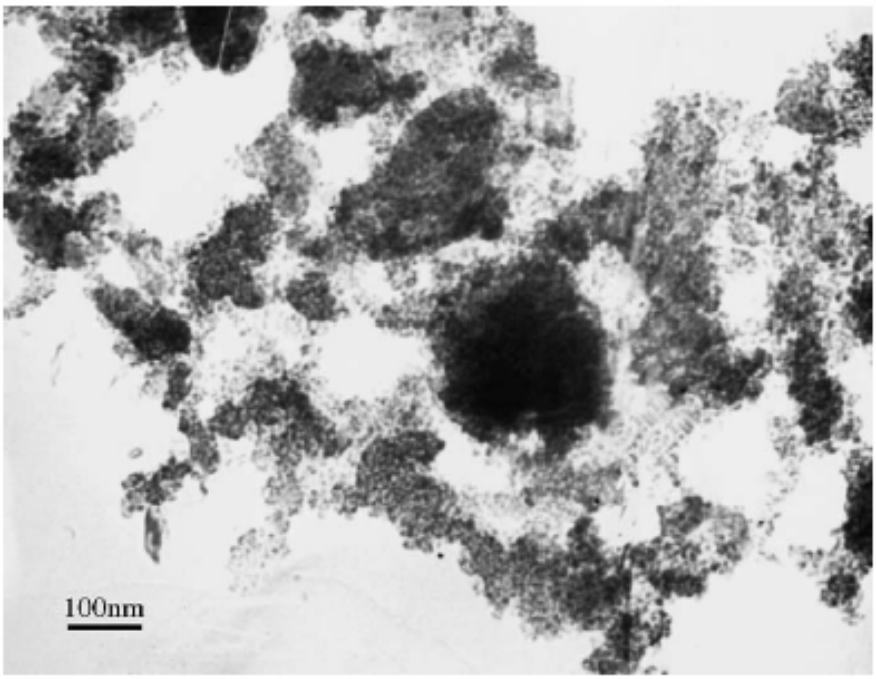


Fig. 1. TEM micrograph of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanocrystalline particles.

CHAPTER-2

CHAPTER OBJECTIVE-

PREPARATION OF MULTIFERROIC COMPOSITES

2. PREPARATION OF MULTIFERROICS

Ceramic composites of Ni0.8Co0.1Cu0.1Fe2O4 and lead-zirconate-titanate were prepared using conventional solid state reaction methods. The presence of constituent phases in composites was confirmed by X-ray diffraction(XRD).The variation of dielectric constant with frequency (100 Hz- 1MHz) and temperature has been studied. The variation of loss tangent (tanΦ) with temperature (at frequency 1 kHz) has also been studied.The magnetoelectric (ME) output was measured as a function of dc magnetic field .The maximum value of ME output (625 Mv/cm) was observed for 25% ferrite +75 % ferroelectric phase .The maximum ME response can be explained in terms of the content of ferrite , permittivity of dielectric material and the intensity of magnetic field. The ME response of these composites was observed to be linear within low dc magnetic field .These composites may form the basis for the development of magnetic sensors and transducers for use in solid state microelectronics and microwave devices.

Preparation of ME composites

The samples were prepared by standard ceramic methods which many advantages over the unidirectional solidification methods .The piezomagnetic ferrite phase was prepared by the solid state reaction using NiO, CoO, CuO and Fe2O3 in molar proportions as starting materials .Similarly the ferroelectric phase was prepared using PbO,ZrO2 and TiO2 in molar proportions .The constituents phases were presintered at 900 degree temperature for 10 hours separately .After presintering , the constituent phases were ground to fine powder . The composites were prepared with compositions (x)Ni0.8Co0.1Cu0.1Fe2O4/(1-x)PbZr0.8Ti0.2O3 where x=0.15,0.25,0.35, and

0.45.These composites were again ground for 3 hours so as to mix them thoroughly . The powder was then pressed in to pellets having diameter of 1.5 cm and thickness 2-3 mm. The palletized samples were sintered at 1000 degree for 12 hours.

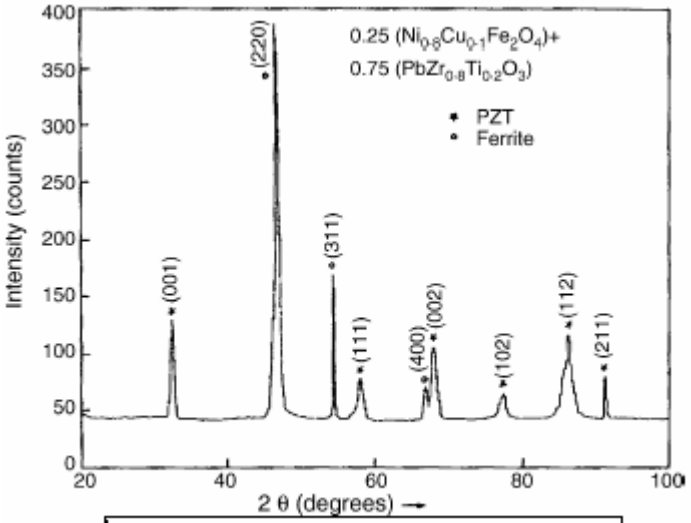


Fig. 2 XRD pattern of composite with $x = 0.25$.

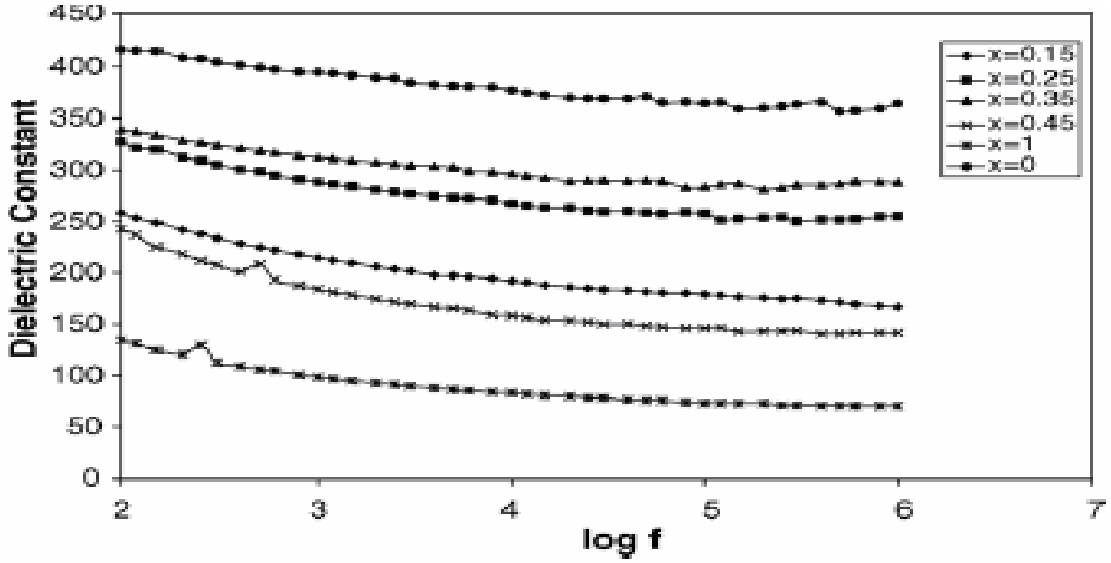
Above is the XRD pattern of composite containing 25% ferrite and 75% ferroelectric phase. It is confirmed that ferrite phase has cubic spinel structure and ferroelectric phase has tetragonal perovskite strucrure.

TABLE-1

Data on structural and dielectric properties of $(x)Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4/(1-x)PbZr_{0.8}Ti_{0.2}O_3$ composites

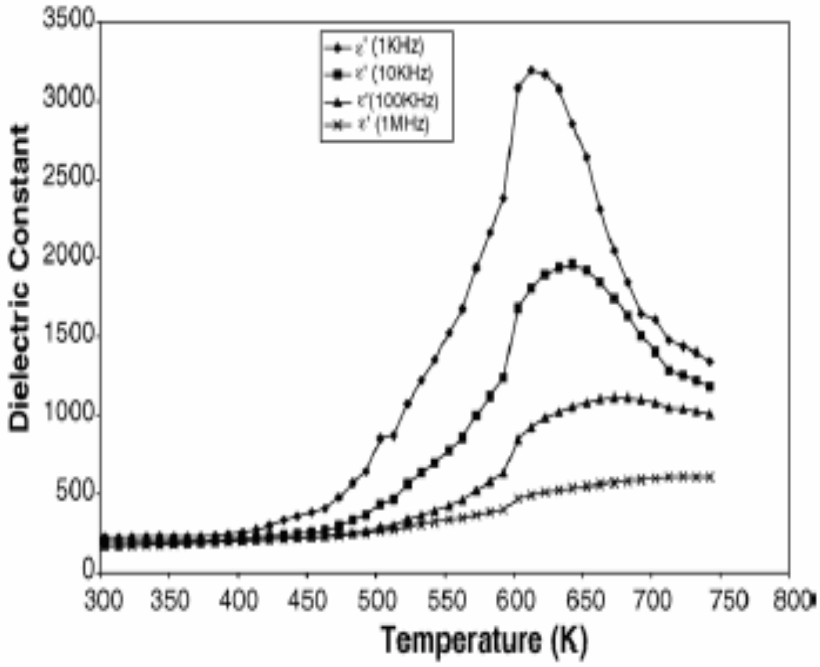
x (mol%)	Lattice parameter, a (Å) (ferrite phase)	c/a ratio (ferroelectric phase)	$\tan\delta_{RT}$ (1 kHz)	ρ_{RT} (Ω m)	ε'_{RT} (1 kHz)	T_c (K)	ε'_{max} (1 kHz)	ME output (mV/cm)
0.00	–	1.056	0.039	3759	394	603	2009	–
0.15	8.231	1.022	0.111	3054	214	613	3192	625
0.25	8.203	1.001	0.077	3511	287	623	3065	513
0.35	8.337	1.015	0.097	3066	312	633	2320	431
0.45	8.337	1.005	0.146	2893	184	643	3174	345
1.00	8.346	–	0.290	2303	98	483	262	–

Variation of dielectric constant with frequency for $x(Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4) + (1 - x)PbZr_{0.8}Ti_{0.2}O_3$ composites.



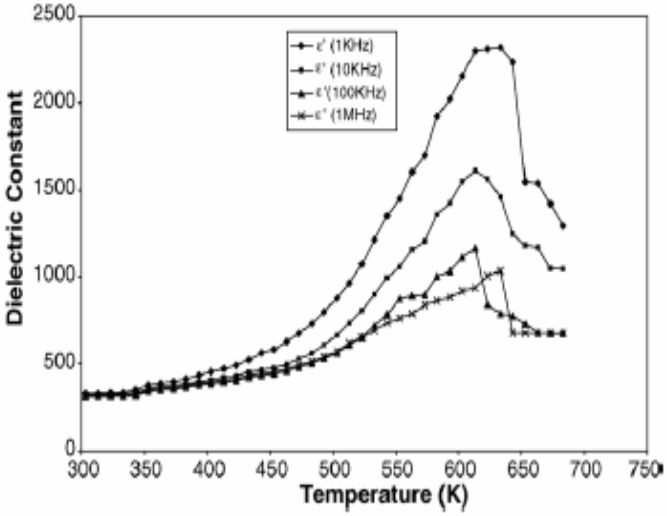
AG-3

Variation of dielectric constant with temperature for $0.15(Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4) + 0.85PbZr_{0.8}Ti_{0.2}O_3$ composite.



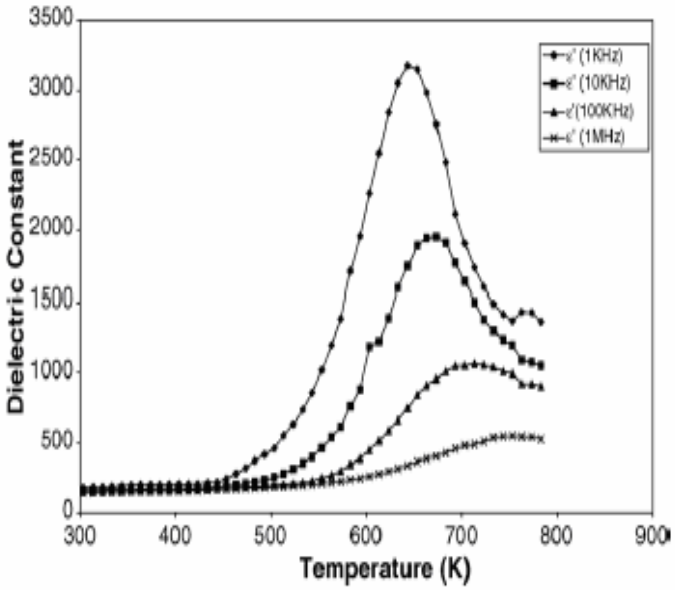
Variation of dielectric constant with temperature for $0.35(Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4) + 0.65PbZr_{0.8}Ti_{0.2}O_3$ composite

figure-4



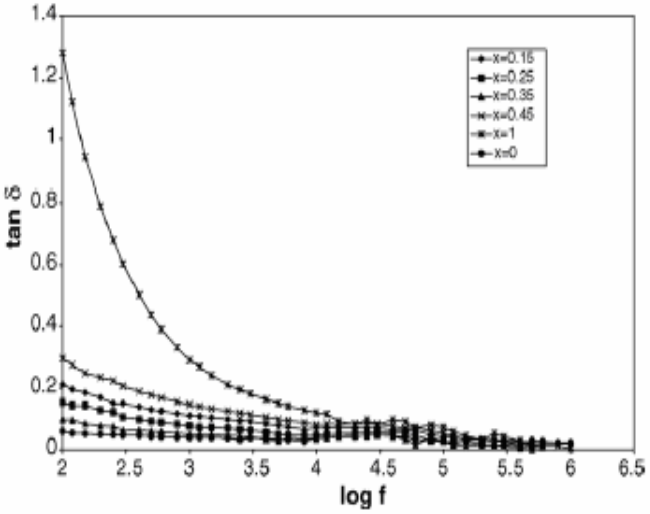
Variation of dielectric constant with temperature for $0.45(Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4) + 0.55PbZr_{0.8}Ti_{0.2}O_3$ composite.

figure-5



Variation of dielectric constant with temperature for $x(Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4) + (1-x)PbZr_{0.8}Ti_{0.2}O_3$ composites at

figure-6



Variation of loss tangent ($\tan\delta$) with temperature for $x(Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4) + (1-x)PbZr_{0.8}Ti_{0.2}O_3$ composites at

figure-7

1kHZ

$Ni_{0.5}Co_{0.5}Fe_2O_4$+$Ba_{0.8}Pb_{0.2}TiO_3$ ME composites

The ceramic method consisting of four steps (i) mixing of powders (ii) presintering (iii) pressing (iv) final sintering was used to prepare ME composites. The polycrystalline BPT Ba0.8Pb0.2TiO3 was prepared following the ceramic route . A.R grade BaO ,PbO , TiO2 were used for the preparation Ni0.5Co0.5Fe2O4 ferrite was prepared using A.R grade NiO , CoO and Fe2O3 in required proportion. The ferroelectric Ba0.8Pb0.2TiO3 and ferrite phase Ni0.5Co0.5Fe2O4 were presintered separately at 900 degree and 700 degree for 12 hours respectively .

Composite sample ferroelectric phase	Compositions
x=0.85	$x Ba_{0.8}Pb_{0.2}TiO_3+(1-x)Ni_{0.5}Co_{0.5}Fe_2O_4$
x=0.70	$x Ba_{0.8}Pb_{0.2}TiO_3+(1-x)Ni_{0.5}Co_{0.5}Fe_2O_4$
x=0.55	$x Ba_{0.8}Pb_{0.2}TiO_3+(1-x)Ni_{0.5}Co_{0.5}Fe_2O_4$

table-2

Above is the ME composition preparation table .The composite mixture was presintered at 800 degree for 12 hours .

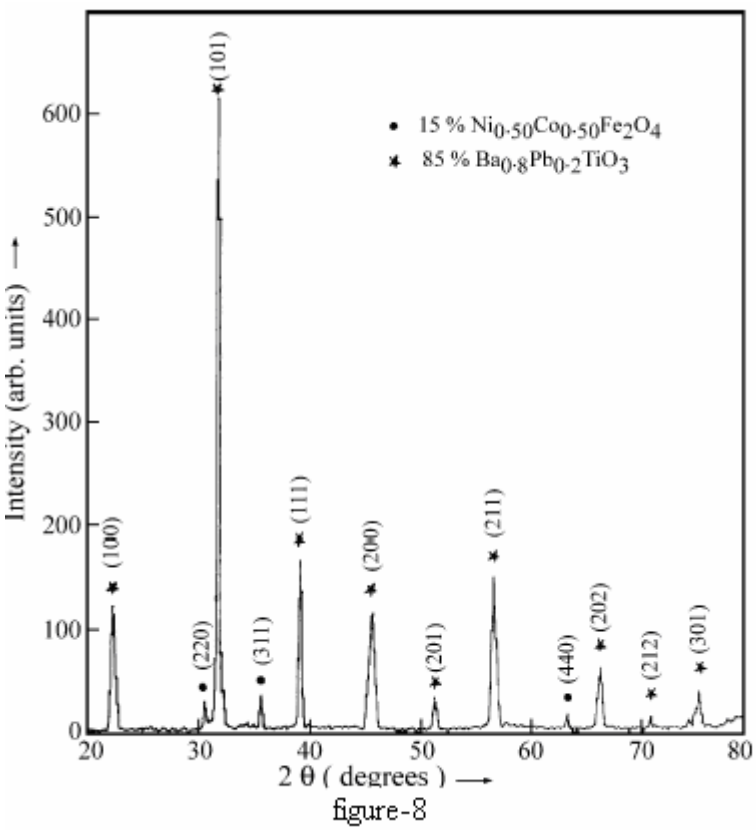


figure-8

XRD pattern of 15% Ni0.5Cu0.5Fe2O4+85% Ba0.8Pb0.2TiO3 Composites

NiCuZn ferrite

$(Ni_{0.2}Cu_{0.2}Zn_{0.6}Fe_{1.96}O_4)$

is prepared using traditional solid state reaction method .The analytical grade NiO , CuO ,ZnO and Fe2O3 provided by Beijing Beihua Fine chemicals Co. Ltd were used as raw materials .

CHARACTERIZATION shrinkage curves were determined by thermo mechanical analyzer .The phase structure is identified XRD..

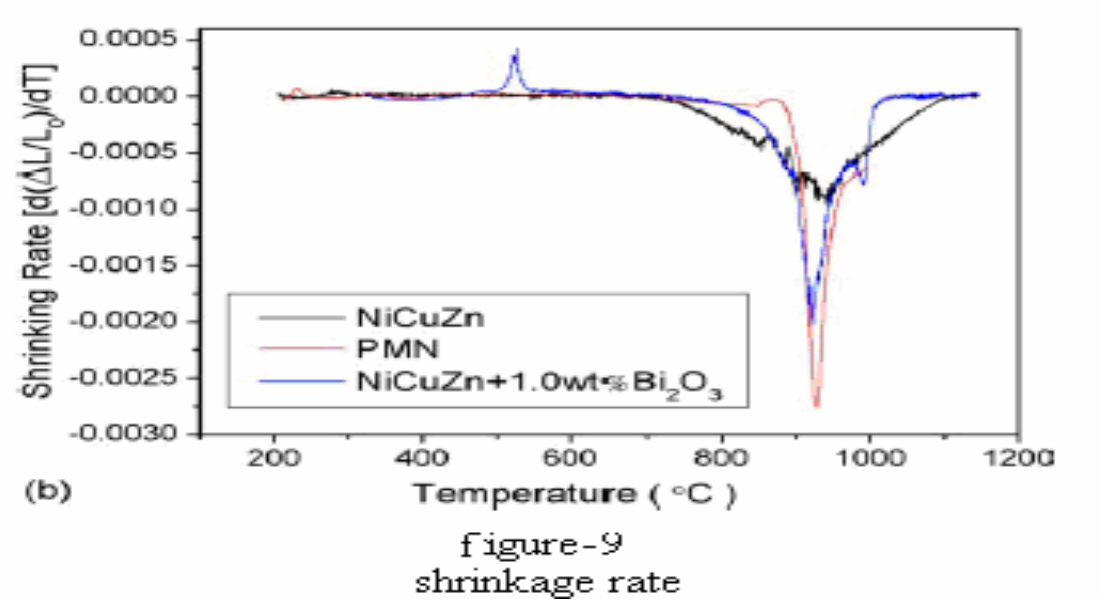


figure-9
shrinkage rate

(A) above is the graph for shrinkage rate

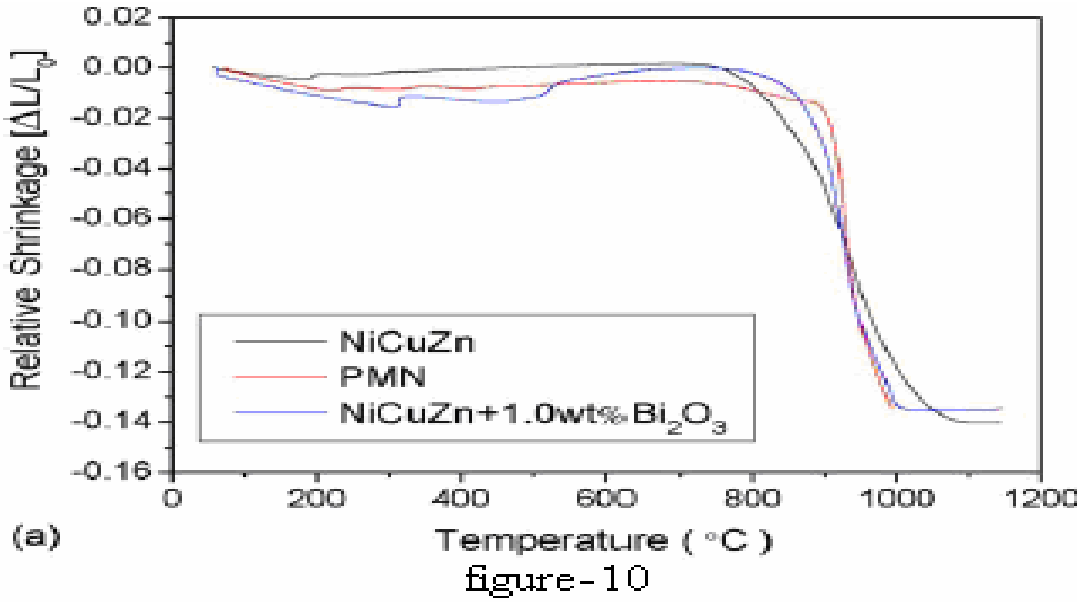


figure-10

(B) shrinkage graph

XRD patterns of the mixture sample ,pure ferroelectrics and ferrite sintered at 950 degree temperature.

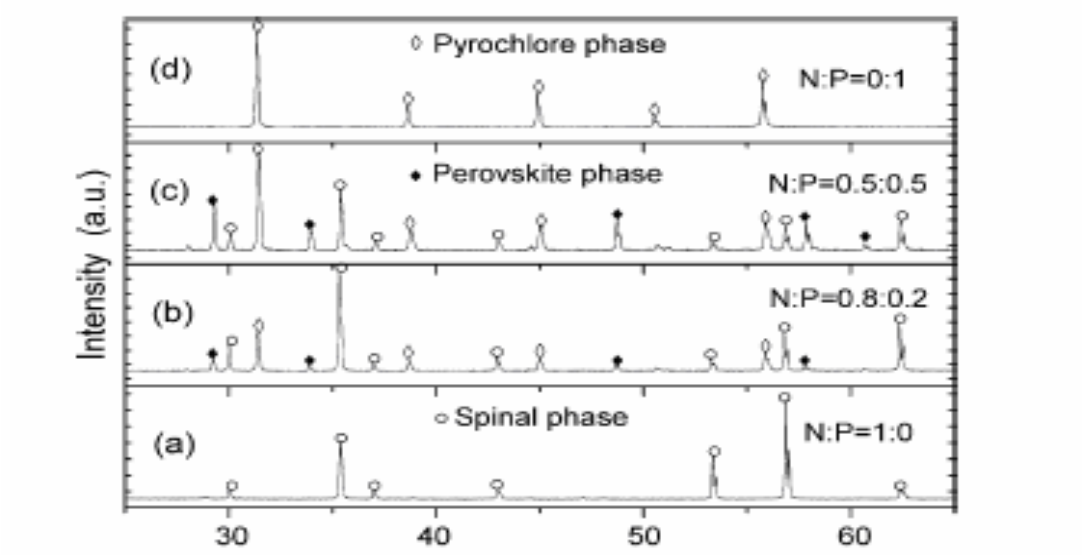


figure-11- phase variations on the basis of intensity variations

Phase analysis

Because the ferrite particles must directly contact the ferroelectric particles, the chemical reactions happened at the interfaces can be investigated by the mixtures of the NiCuZn ferrite powders and PMN ferroelectric powders. So the 50/50 wt % mixture NiCuZn ferrite and PMN ferroelectrics was prepared and sintered at 950 degree centigrade for 4 hours ..

Composition ferrite and ferroelectrics

Ferrite	Ferrite - Ferroelectric composite					
	Composition(1-y) of Ferrite in mole fraction			Composition (y) of $Ba_{0.8}Pb_{0.2}TiO_3$ in mole fraction		
$CuFe_2O_4$	0.15	0.30	0.45	0.85	0.70	0.55
$CuFe_{1.8}Cr_{0.2}O_4$	0.15	0.30	0.45	0.85	0.70	0.55
$CuFe_{1.6}Cr_{0.4}O_4$	0.15	0.30	0.45	0.85	0.70	0.55
$MnFe_{1.8}Cr_{0.2}O_4$	0.15	0.30	0.45	0.85	0.70	0.55
$MnFe_{1.6}Cr_{0.4}O_4$	0.15	0.30	0.45	0.85	0.70	0.55

table -3 **XRD OF 70% $Ba_{0.8}Pb_{0.2}TiO_3$ COMPOSITE**

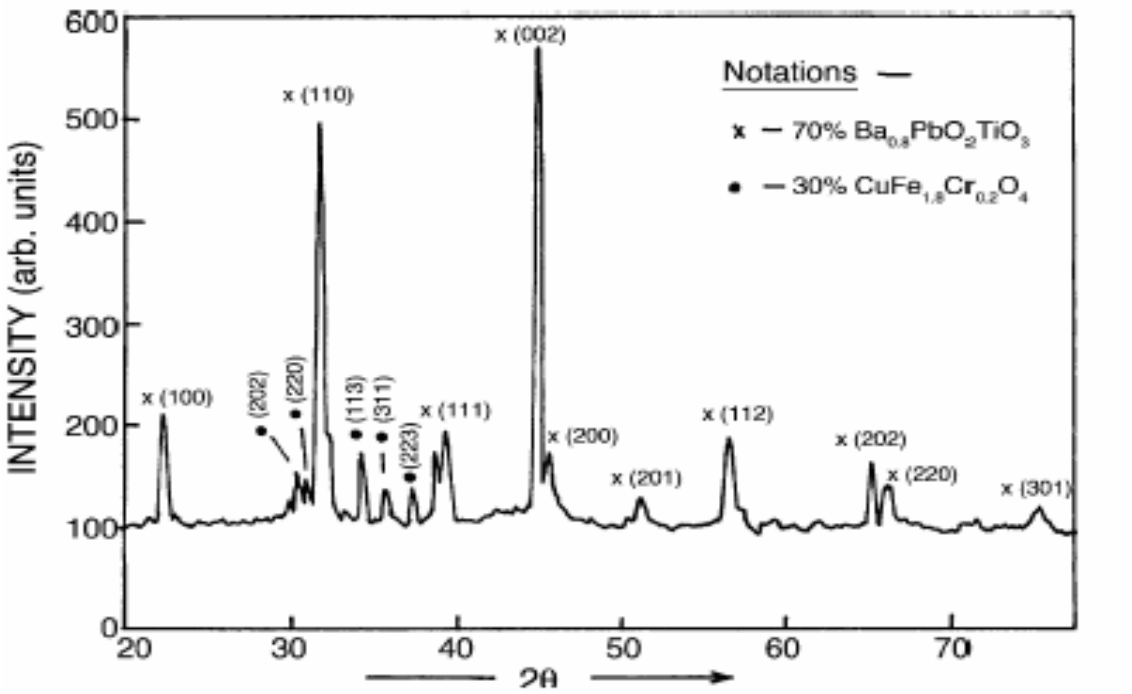


figure-12 : XRD patterns obtained from the sintered materials

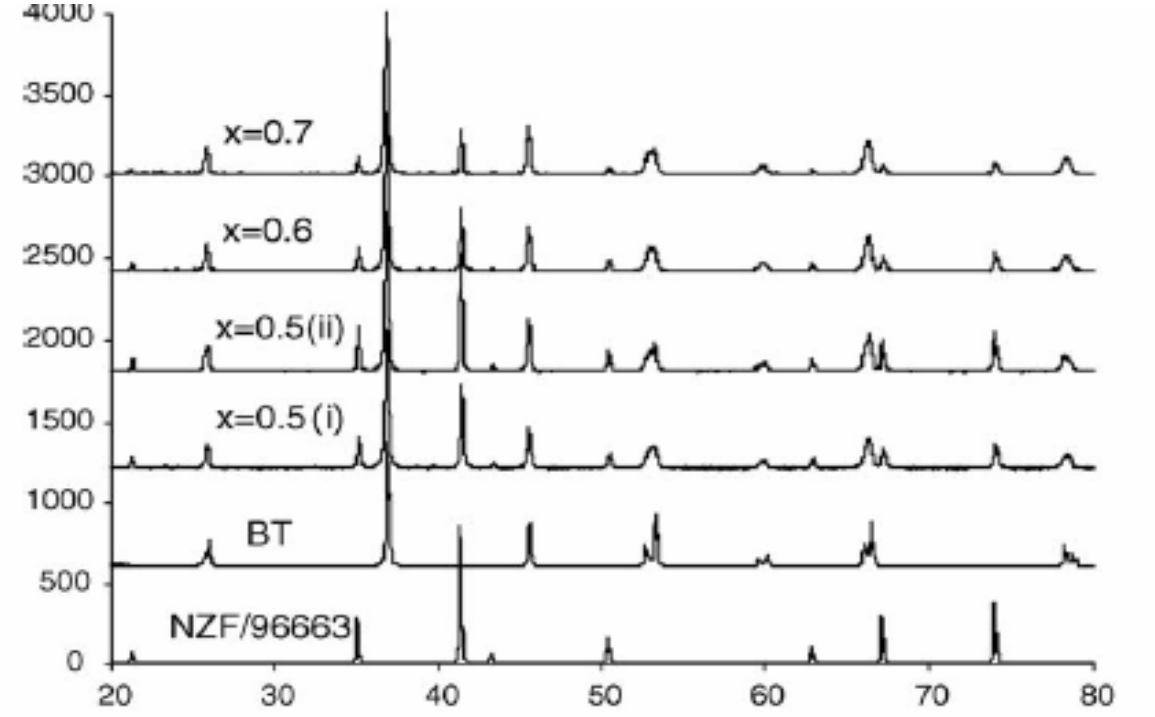


figure-13 XRD patterns obtained from sintered material

Preparation of multiferroic composites of BaTiO3-Ni0.5Zn0.5Fe2O4

Ceramic composites of xBaTiO3-(1-x)Ni0.5Zn0.5Fe2O4 (BT-NZF) with x=0.5,0.6 and 0.7 were prepared using two different procedures (i) by mixing BT powders and NZF powders and (ii) by coprecipitating Fe^{iii}-Ni^{ii}-Zn^{ii} nitric salts in NaOH solution in which the BT powders were previously dispersed.

(a) mixed powders method -- BT powders were prepared via solid state reaction from BaCO3 and TiO2.The precursors were mixed for 48 hours, freeze dried , thermally treated at 1100 degree centigrade for 4 hours and the resulting BT powders were milled and sieved at 50 micro meter . NZF powders were prepared by co precipitation method at room temperature of stoichiometric amounts of Zn(NO3)2.6H2O(Aldrich), Ni(NO3)2.6H2O (Aldrich) and Fe(NO3)2.6H2O(Aldrich) solution with NaOH solution .The resulting gel was washed several times with water , freeze – dried and calcined for 1 hour at 400 degree centigrade to promote the formation of the NZF phase . The powders of BT and NZF in desired proportion (x=0.5, 0.6 ,and 0.7 wt %)

were milled together , isostatically pressed and sintered at 1050-1150 degree centigrade for 1 hour.

(b) **Coprecipitaion method** the BT powders were prepared according to the procedure described above , were maintained in suspension I NaOH solution by sonication and vigorously stirred . The nitrication solution was added quickly to the alkaline suspension using the same concentration, precursors and molar OH/NZF ratio described above . The resulting suspension was washed several times with water and trice with acetone. The powders were recovered by filtration , dried at 60 degree centigrade and calcined for 1 hour at 400 degree centigrade to promote formation of the NZF phase . The mixture was manually milled in agate mortar , iso statically pressed and sintered at 1050-1150 degree for 1 hour. in case of simple mixing of NZF and BT powders , poor densification and homogeneity of the sample with large aggregates of NZF octahedral crystals and large pores were found in some regions , in spite of good initial mixing of two phases.Since an increase in of the sintering temperature to achieve better densification would case reactions at the interfaces , the co precipitation method was adopted for improving the microstructures .

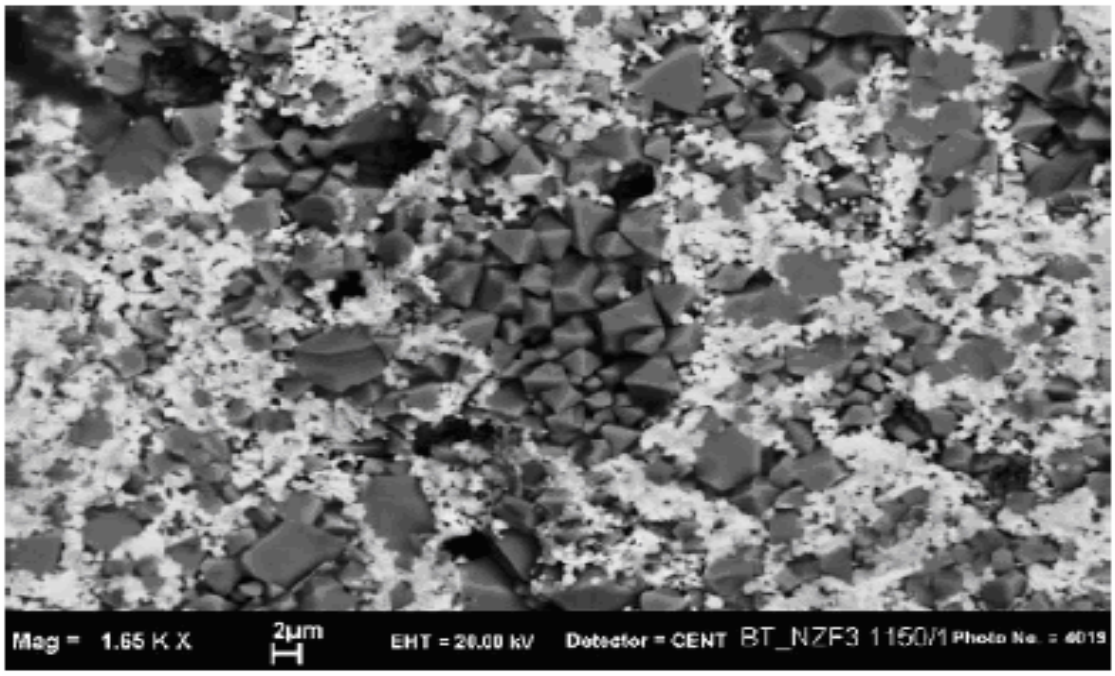


figure-14

Backscattered SEM image of a fracture surface of a 0.5BT-0.5NZF sintered Body prepared by mixed powder method

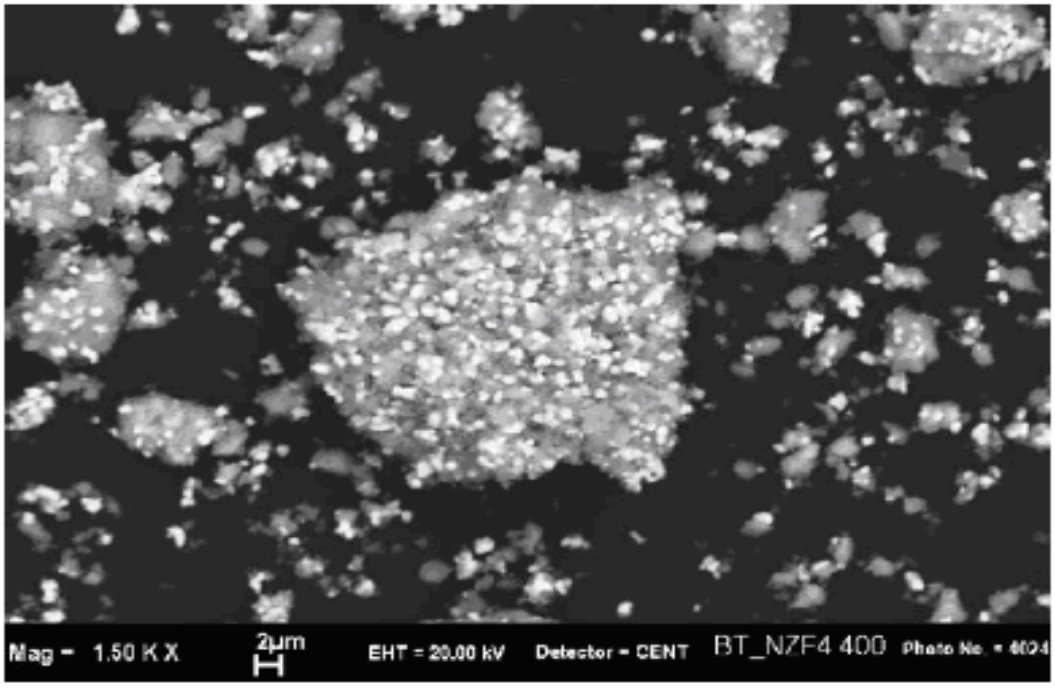


figure-15

Above is the SEM image of the BT-NZF powders after calcinations at 400 degree centigrade up to 1 hour(white grains :BT ,grey matrix spinel NZF)

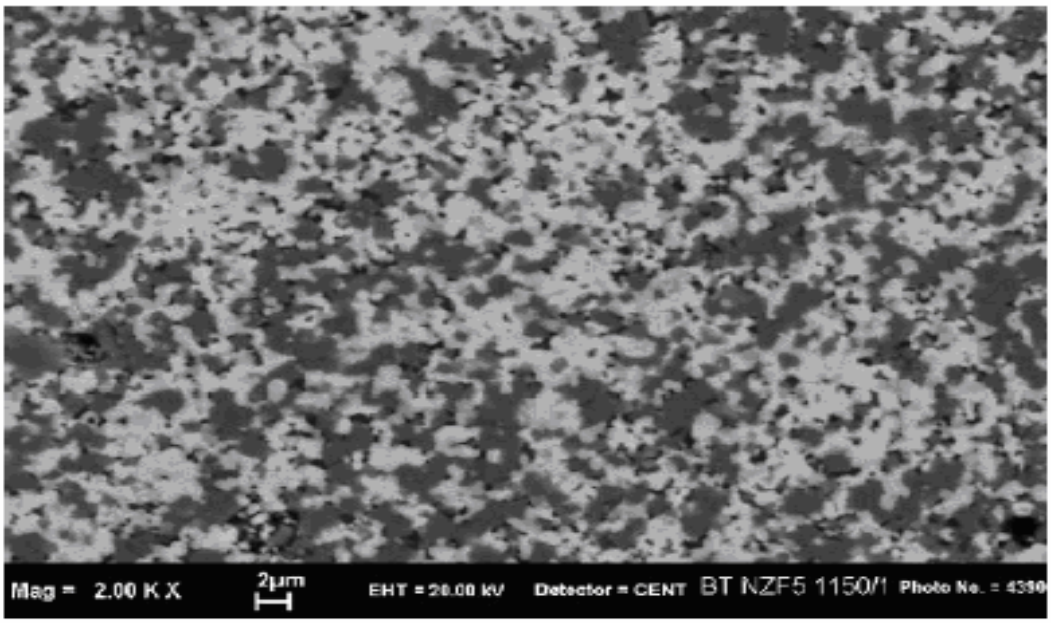


figure-16

(**Back scattered image (SEM) of a polished surface of a composite ceramic 0.6BT-0.4NZF prepared by co-precipitation (white grains correspond to the pervoskite BT phase , grey grains to the NZF spinel phase**)

Spinel- perovskite nanocomposites of xCuFe2O4-(1-x) BaFeO3 with x=0.1 , 0.2 .0.3 and 0.4 were prepared using water soluble inorganic salts. All chemicals used in the experiments were of analytical grade. Ferric nitrate Fe(NO3)3.9H2O copper nitrate Cu(NO3)2.3H2O and bismuth nitrate Bi(NO3)3.5H2O , citric acid and ethylene glycol were used as starting materials . Appropriate molar proportion of metals nitrates was fixed at Cu:Bi:Fe ratio of 1:9:11, 1:4:6 , 3:7:13 and 1:1.5:3.5. An aqueous solution of citric acid was prepared in distilled water . Then ferric nitrate and bismuth nitrate were prepared in turn with constant stirring at 50- 60 degree centigrade to avoid precipitation and obtain homogeneous mixture.

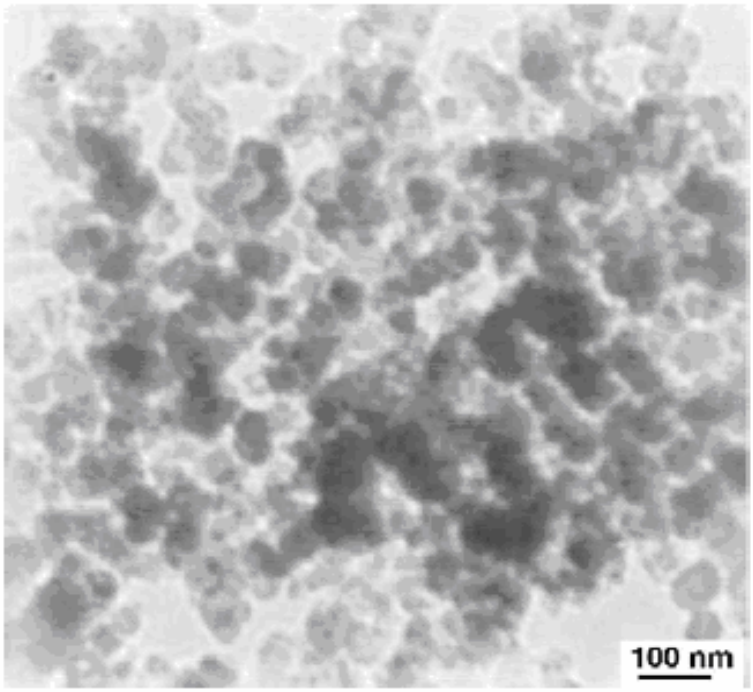


figure-17

TEM OF 0.3CuFe2O4-0.7BiFeO3 Powder annealed at 500 degree centigrade

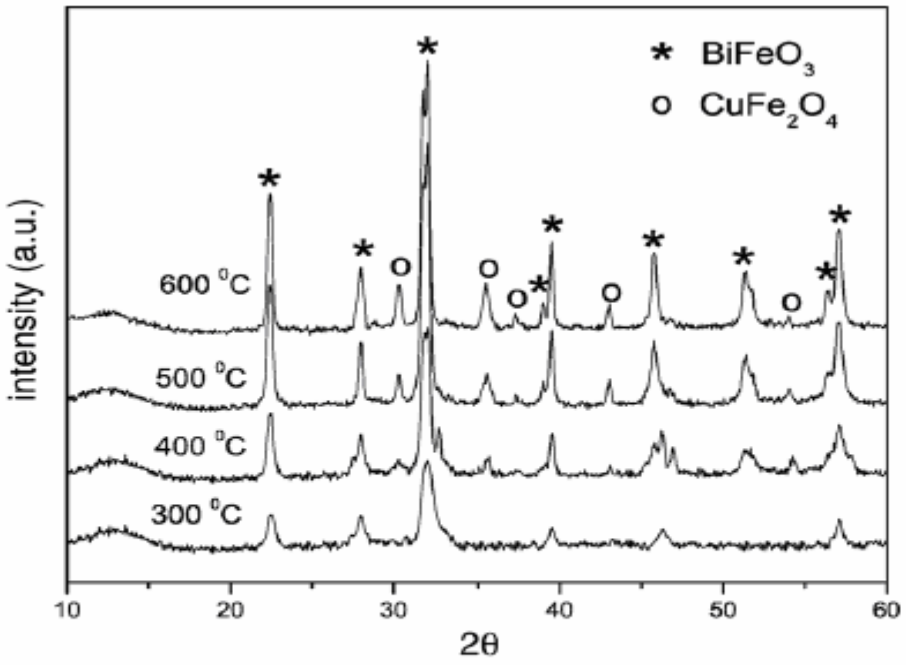


figure-18

XRD pattern of 0.2CuFe2O4-0.8BiFeO3 powder annealed at different temperatures for 2 hours which shows that composite consisting of Cu2Fe2O4 and BiFeO3 has formed after being annealed at 500 degree centigrade..

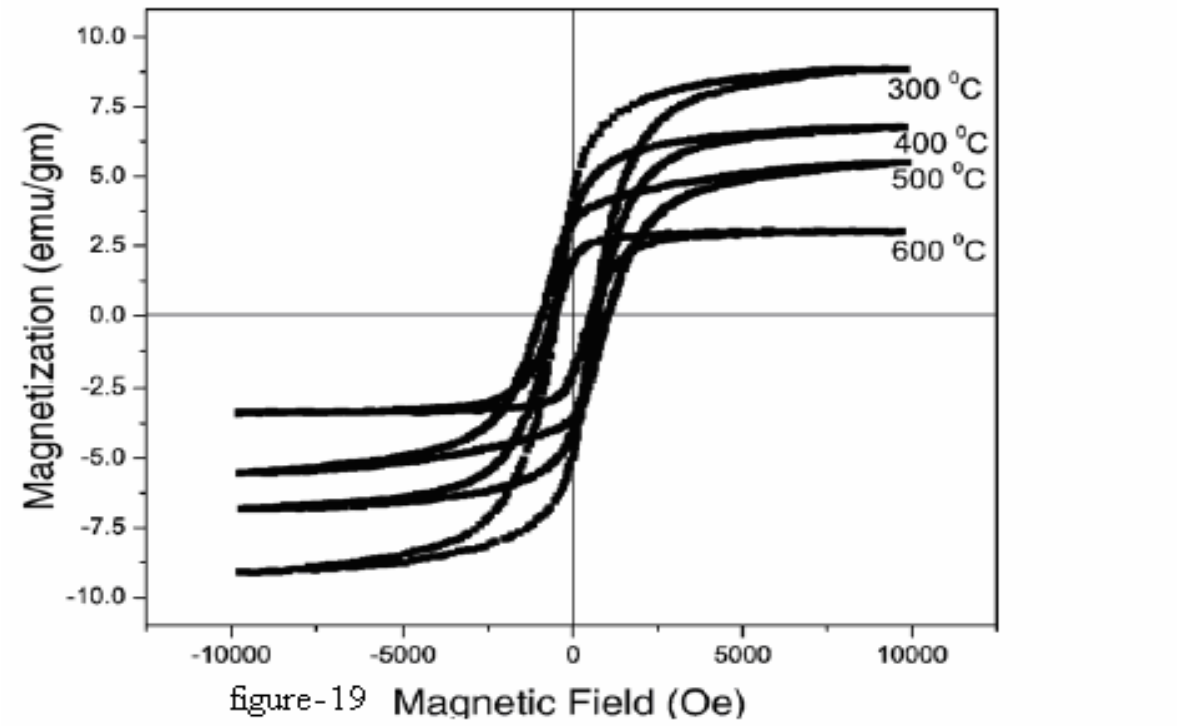


figure-19

Above is the hysterisis loop of 0.2CuFe2O4-0.8BiFeO3 sample annealed at different temperatures

PREPARATION OF MIXED COMPOSITION POWDERS

The mixed composition powders were prepared either by ball milling or by grinding in a mortar . For both methods , the pure powders were used had a characteristics grain size and did not contain binders.

Ball milling method two wt% of the binders Mobil CERQ(based on vax microemulsion) was added and the powders were ball milled in demineralized water for 4 hours . The powders obtained were dried at 100 degree centigrade in a drying oven . The mixed composition powders were then ready to be used for the preparation of the multilayer for characterization .

Grinding

The first step was to ball mill separately the dielectric powder and the ferrite using the conditions described above. Then the two powders were ground together in a mortar

characterization

mixed composition powders

the first step was of characterization of the mixed composition powders was to obtain their X-ray diffraction patterns. In this way the composition of the ceramics is controlled .

mixed composition ceramics

X-ray diffraction patterns were obtained for each ceramics in order to check the composition and to detect whether a chemical reaction had taken place during the sintering. Some physical properties of the ceramics were also measured : the density using Archimedes method in water , the grain size using SEM, thermal expansion coefficient using dilatometry and the permittivity using a capacitance range bridge.

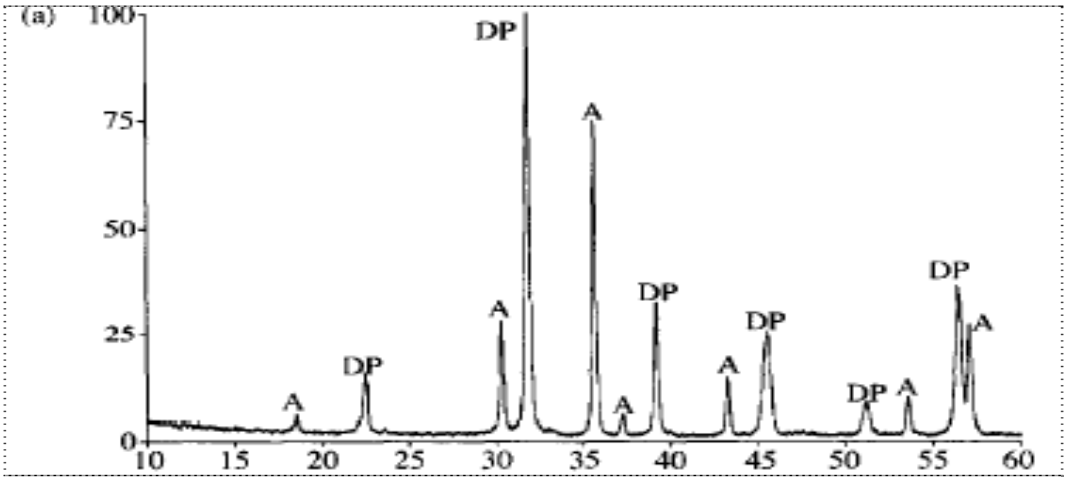
Fabrication of multilayers

The multilayers were fabricated using dry pressing . the following multilayers used were in a first step.

1- ferrite A and DP with MPB(mixed powder composed of 50% of ferrite A and 50% of DP) as an interlayer.
2- Ferrite B and DP with MPBB(mixed powder composed of 50% of ferrite B and 50% of DP) as an interlayer. In second step , two other multilayers were prepared

Characterization of multilayers

In order to obtain information on thermal cracking, SEM was performed with a low vacuum microscope where the samples do not need to be coated.



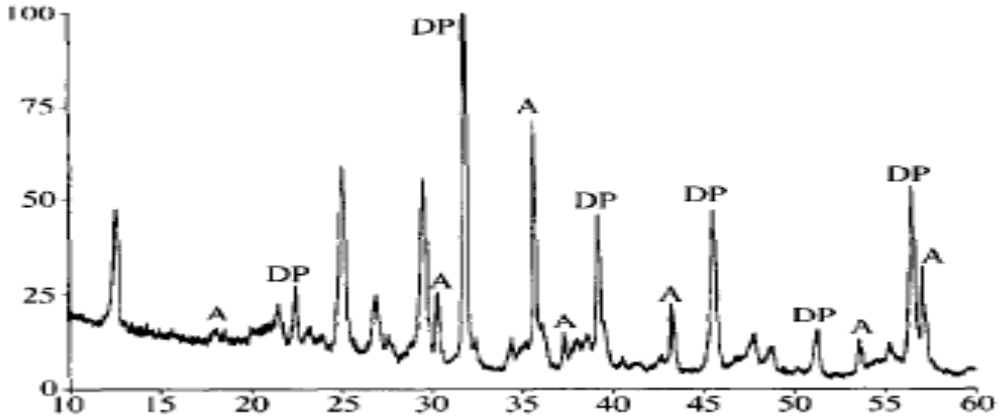
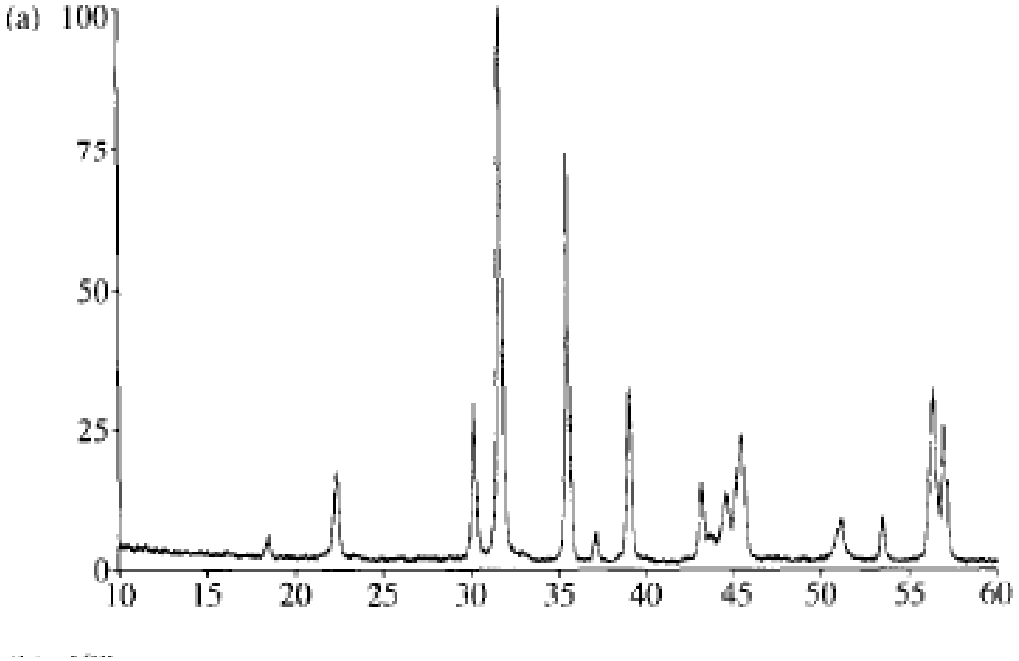


figure-20

X-ray diffraction patterns of (a) MPB powder and (b) ceramic.



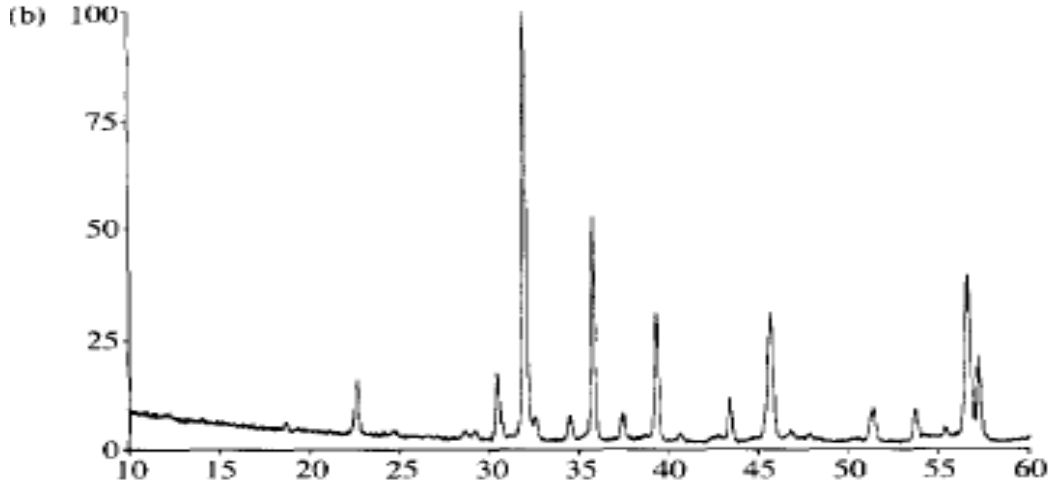


figure-21

X-ray diffraction patterns of (a) MPBB powder and (b) ceramics

CHAPTER-3

CHAPTER OBJECTIVE

PROPERTIES OF MULTIFERROIC COMPOSITES

3-PROPERTIES OF MULTIFERROIC COMPOSITES

Perovskite-type multiferroic materials (BiFeO3, BiMnO3, and YMnO3) show ferroelectricity and ferromagnetism at a time ferroelasticity too.these materials because of these multitype characteristics can be used in magnetoelectric devices where both polarization and magnetization can be coupled. the presence of impurity phases, leakage currents , and pores in bulk BiFeO3 ceramics can be described by following mechanism .

$$\begin{aligned} Bi_2O_3 + Fe_2O_3 \Rightarrow (2/x)Bi_xFe_yO_{1.5x+1.5y}(x>y) + \\ (1-y/x)Fe_2O_3 \quad [\text{no reaction}], \end{aligned} \tag{1}$$

$$\begin{aligned} Bi_2O_3 + Fe_2O_3 \Rightarrow 0.5Bi_2Fe_4O_9 \\ + 0.5Bi_2O_3 \quad [\text{no reaction or volatilization}]. \end{aligned} \tag{2}$$

$$2Fe^{3+} + O^{2-} \Rightarrow 2Fe^{2+} + 0.5O_2[\text{volatization}] + V_O^{2+}, \tag{3}$$

$$2Bi^{3+} + 3O^{2-} \Rightarrow Bi_2O_3[\text{volatilization}] + 2V_{Bi}^{3-} + 3V_O^{2+}. \tag{4}$$

$$\begin{aligned} 2Bi_xFe_yO_{1.5x+1.5y-\delta} + \delta O_2 \Rightarrow xBi_2O_3[\text{volatilization}] \\ + yFe_2O_3. \end{aligned} \tag{5}$$

Equations 1 and 2 state that if insufficient reactions of Bi2O3 and Fe2O3 powders occur as a result of inadequate mixing of powders , improper use of sintering method or process. Volatilization of Bi2O3, etc. It will be difficult to keep the stoichiometry of BiFeO3 ceramics, multiphase samples consisting of unreacted oxides (Bi2O3 and Fe2O3) and other impurities with chemical formula of $Bi_xFe_yO_{1.5x+1.5y}$(x=!y).

Six different types of $BiFeO_3$ ceramic samples denoted as BiFeO3—1, BiFeO3-2, BiFeO3—3……BiFeO3-6. BiFeO3-1 shows single phase , high resistivity and

low porosity . as these are the preconditions for imparting high polarization and hence measuring multi properties.

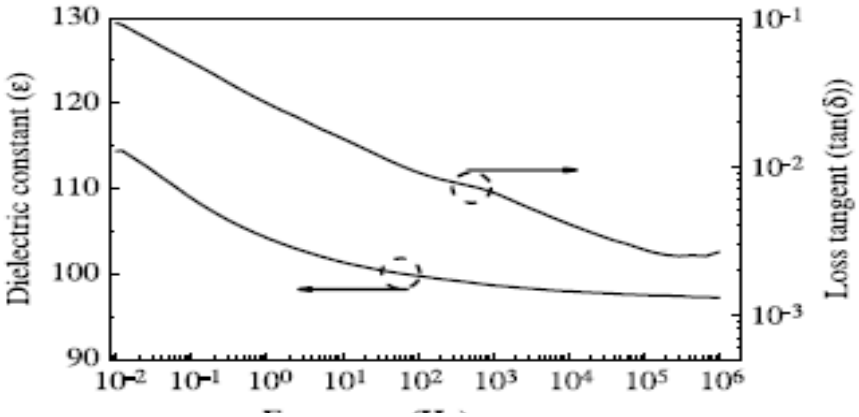


figure-22 For BiFeO3—1

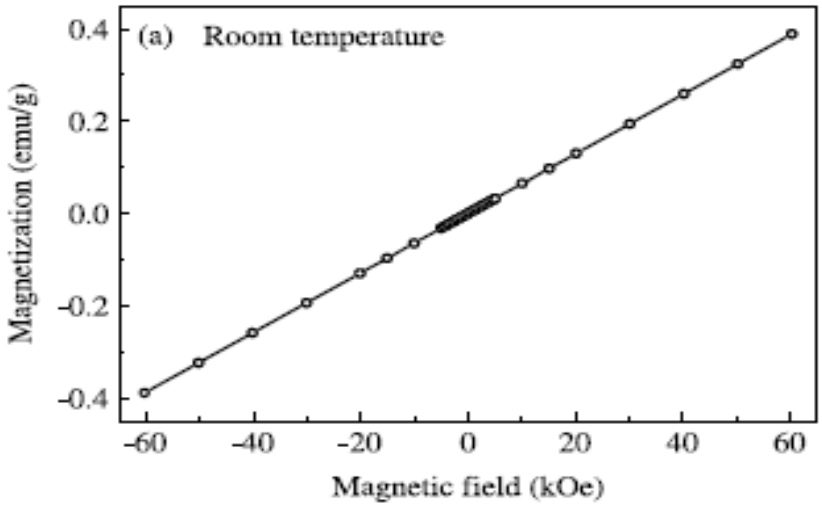


figure-23 BiFeO3-2

Six different types of BiFeO3 ceramic samples have been synthesized to investigate the factors that govern the formation of poreless, low resistive and single phase multiferroic BiFeO3 ceramics. It has been shown that single phase BiFeO3 samples with electrical resistivity as high as $5\times10^{12}\Omega$ cm and porosity as low as 8% can be synthesized by using Bi2O3 powders of <1 μm size and a rapid liquid-hase sintering process of 855^0C for 5 min at 100 degree centigrade /second . These single phase samples also demonstrate a large saturation polarization of $16.6\mu C/cm^2$ and a low leakage current density of $30Ma/m^2$, together with large piezoelectric constant.

The multiferroic material $CdCr_2S_4$ shows coexistence of ferromagnetism together with magnetocapacitive effect. The complex dielectric permittivity of this compound and of

the structurally $CdCr_2S_4$ was studied by means of broadband dielectric spectroscopy using different electrode materials .

$CdCr_2S_4$ and $CdCr_2Se_4$ canonical ferromagnetism coexists at sizable ordering temperatures with relaxor-ferroelectric state , characterized by a significant relaxational behavior. Both order parameters are strongly coupled . there is radical change of the dielectric relaxational dynamics driven by the onset of magnetization that leads to observed strong increase of the dielectric permittivity in these compounds . the present dielectric experiments can not provide final evidence on the microscopic origin of this puzzling behavior. While contact effects could be ruled out and the influence of charge transport seems unlikely a scenario in which the relaxation mechanism interacts with magnetic order via exchangestriction can be considered the most plausible.

As the multiferroic materials coexist magnetic and electric ordering . the interaction of magnetic and electric sub systems manifests itself as magnetoelectric (ME) effect that is interesting for practical applications such as the sensor techniques , micro electrics and magnetic memory systems . It was found that the magnetoelectric interaction enables to control the spatially modulated spin structure with electric field . the influence of electric field on the magnetic phase is considered . The phase diagrams in the magnetic field – electric field co-ordinates are calculated .

The dielectric properties of $TmFe_2O_4$: Magnetization measurement shows a ferromagnetic transition around 240 K. A modulation of this ordering with a slow spin relaxation found below 70 k-100 K. A characteristic low frequency dielectric dispersion was also obtained , which is analogous behaviour to that for a few other RFe2O4 oxides reported previously..

CHAPTER 4

APPLICATIONS OF MULTIFERROICS

3- **APPLICATIONS** --

Multiferroic composites, because of magnetic and electric coexisting properties are widely applicable…

The multifunctional materials combining several properties in the same phase showing new and enhanced properties are widely used in scientific and technological fields. They are widely applicable in fundamental physics and attractive as sensors and transducers in radio-,opto- and microwave electronics and instrumentation. The ME effect adds a supplementary degree of freedom in designing materials. For new applications , opening the possibility to manipulate the magnetic properties through electric fields and etc.

CHAPTER -5

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