

Preparation and Characterization of BNT-BT-NZFO ME composites

Dissertation submitted in fulfillment of the requirements for the Degree of

MASTER OF TECHNOLOGY

By

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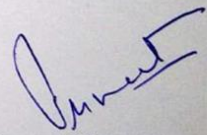
I hereby certify that the work which is being presented in this report entitled, "**Preparation and characterization of BNT-BT-NZFO ME composites**" as a part of curriculum during **Master of Technology in Material Science and Metallurgy**, submitted to **School of Physics & Material Science of Thapar University, Patiala**, is an authentic record of my own work carried under the supervision of **Dr. Puneet Sharma, SPMS**. It refers others researcher's work which are duly listed in the reference section. The matter contained in this report has not been submitted, neither in part or in full to any other degree to any other university or institute except as reported in text and references.

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ACKNOWLEDGEMENT

I would like to thank **Dr. Puneet Sharma**, Associate Professor (SPMS), for giving me a chance to work under his supervision, without whose help and constant guidance this thesis would have not taken shape. I am extremely thankful to **Dr. O. P. Pandey**, Dean of Research, for their co-operation and encouragement. I am also thankful to all staff members of SPMS, for their constant cooperation in experimental work. I am special thankful to Dr. Kulveer Singh for providing me characterization facilities for Dielectric Measurements.

I am highly thankful to my senior Dr. Mintu Tyagi and PhD scholars Chhavi Pahwa, Shivani Jindal, Santhosh Kumar Mahadevan, and Anoop Partap Singh who provided their valuable guidance and suggestions during the course of the work. I acknowledge and thank my elders and my friends for their support and motivation. I am very thankful to my parents and brother for their constant cooperation, inspiration, patience, blessing and moral support.

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ABSTARCT

In recent years, Multiferroics are the most interesting topic in the research because of its application in hard disk drives, permanent magnets, transducers and surface acoustic wave (SAW) devices. It shows high piezoelectric coefficient, high chemical stability and good magnetic properties. More work is done on lead based ferroelectric oxides e.g. PZT for synthesis of *ME* composites but due to their toxic nature nowadays researchers paid more interest to Non-Lead based ME coupled composites. Ba(ZrTi)O₃ (BZT), BaTiO₃ (BT), BFO and BNT are main piezoelectric materials which were used for preparing non lead based Magnetolectric composites. Therefore, In the present work, (1-x) BNT-BT- xNZFO composites were prepared by Sol Gel method. The main focus was to investigate structural, dielectric, ferroelectric and magnetic properties of non lead based magnetolectric composites

Chapter I

INTRODUCTION

Overview

This chapter reviews the basic concepts of Multiferroic materials, their classification and Multiferroic composites which are further classified into two types Lead based and non-lead based composites. Detailed description of basic features and applications of Multiferroic composites included in this chapter. The aim of the work is discussed at the end of this chapter.

Multiferroic materials:

The materials, which simultaneously possess more than one of the ferroic order parameters like ferroelectricity, ferromagnetism and Ferroelasticity, are termed as “**multiferroics**” [1-5]. The materials having piezoelectric as well as ferromagnetism behavior are in great demand. Recently, they have gained much attention and provoking research activity due to their great demand in multifunctional devices like transducers, sensors and spintronics devices etc. [3-7]. Usually a spatial class of materials exhibits the ferroelectric and ferromagnetic order simultaneously [2, 3]. Basically, the ferroelectricity is the property of materials which contain spontaneous stable electric polarization behavior which is switchable in presence of an applied electric field are called ferroelectric materials [2, 4]. On the other hand the ferromagnetism contain the stable magnetization and the magnetic dipoles can be switched by the external applied magnetic field are called the ferromagnetic materials. In recent years, the term ‘**Multiferroic**’ is also extensively used for the materials in which ferromagnetism and ferroelectricity coexist in the same phase as well as the multiphase artificial composite type materials [8-13].

Moreover, an huge interest has been paid to **Multiferroic Magnetolectric (ME)** materials not only because they exhibit simultaneously both ferroelectric/piezoelectric and ferromagnetic properties, but also a coupling interaction between the different orders lead to additional functionalities called as *ME* effect [6, 7]. In these materials the observation of *ME* coupling implies that not only the magnetic field controls the magnetic spins but also the applied electric field can switched the electric dipoles as well as the magnetic spins. This functionality offer an attracted renewed interest for Multiferroic *ME* materials from the view point of current research for several scientific as well as technological importance [5-13].

The pictorial representation of Multiferroics has been depicted by different authors [1, 2] and the concept is shown in fig1. Multiferroic are represented by violet hatching and ME coupling is shown by red hatching in **Fig1.1**

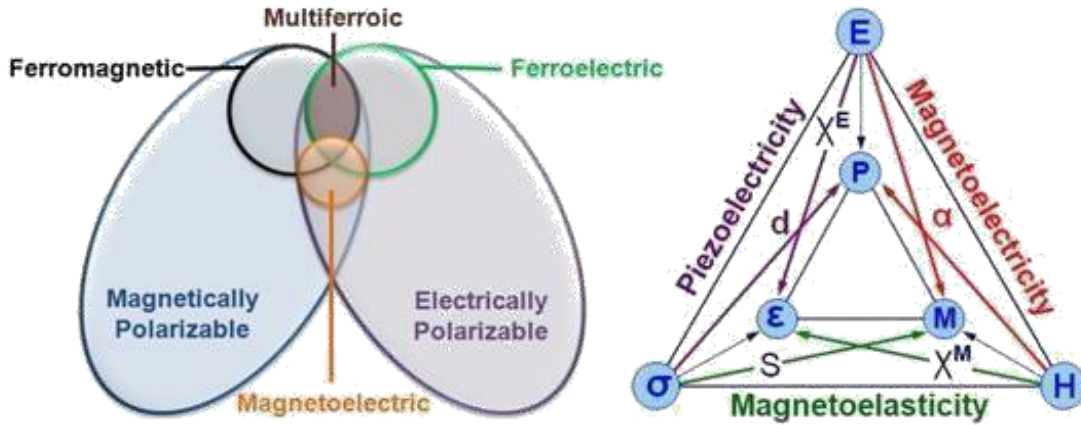


Fig.1.1 The relationship between the Multiferroic and Magnetolectricity

1.2 Classification of Multiferroic materials

The *ME* coupled materials is divided into two groups

- Single phase multiferroics
- Composite type multiferroics

1.2.1 Single phase Multiferroics

So far, many compounds which are single phase Multiferroic *ME* materials such as BFO and rare-earth magnetite has been reported [14-20]. However, all the single phase Multiferroic materials are not very much useful for the technical importance because of anti-ferromagnetic nature and their associated Neel temperature much below the room temperature [18, 19, 20]. The single phase multiferroics are divided in two types. **The type-I Multiferroic** materials contain Perovskite compounds with independently originating ferroelectricity (cations at A-site) and ferromagnetism (cations at B-site). BiFeO_3 , YMnO_3 , BiMnO_3 are the examples of type-I Multiferroic materials [14-20]. **The type II Multiferroics** includes the materials exhibiting rather low ferroelectric as well as magnetic transition temperatures which exclude their applications in Multiferroic devices. TbMnO_3 and TbMn_2O_5 , a Perovskite having anti-ferromagnetic ordering at $T_N = 41\text{K}$ and the second magnetic transition at $T_N = 28\text{K}$ are examples of type II multiferroics [21, 22]. These materials also exhibit strong magneto-electric coupling at low temperature.

1.2.2 Multiferroic magneto-electric composites

Despite the ongoing research on single phase Multiferroic materials, their small magneto-electric coupling coefficients and low working temperature has limited their applications which motivated the design of artificial Multiferroic *ME* composites. In Multiferroic *ME* composites, where an artificial coupling is engineered between the two ferroic order parameters like ferroelectric/piezoelectric and ferri/ferromagnetic phases at room temperature are of particularly interest and ready for technological applications in multifunctional devices. Moreover, Multiferroic *ME* composites consisting of Perovskite based ferroelectric/piezoelectric and spinel ferrites based magnetostrictive constituent provide great design flexibility and better control over the parameters affecting the Multiferroic behavior. Several investigations based on ferroelectric/piezoelectric-ferrite based Multiferroic *ME* composite has been reported [10, 11, 13]. Based on materials the Multiferroic *me* composites can be classified.

1.3 Classification of Multiferroic *ME* composites

Broadly, based on materials, the Multiferroic *ME* composites can be divided into different categories

- Lead based *ME* composites
- Non lead based *ME* composites

Lead based *ME* composites

High dielectric constant and piezoelectric coefficient of lead based ceramics makes them suitable for piezoelectric components for *ME* coupled composites.[10-12]Lead based PZT is extensively studied as *ME* coupling material. However, Pb is a toxic in nature and presents an environmental problem. Thus, in order to toxicity of lead, the interest of researchers is now shifted towards the non lead based materials which used for preparation of *ME* coupled composites.

Non lead BNT based ME composites

For the preparation of Multiferroic materials like BNT based ferroelectric/piezoelectric materials recently have been focused to replace toxic lead based piezoelectric materials. However, it is difficult to match high electromechanical coefficient and high piezoelectric coefficient of lead based PZT with non lead based composites [23]. For the better performance of ME coupled composites, the magnetic components are selected on the basis of chemical stability, Magnetostriction, permeability and resistivity. For this the Spinel ferrites (NFO, CFO) have been used because of high Magnetostriction coefficient and good chemical stability [24-27] In addition to high Magnetostriction coefficient as well as piezoelectric response some other factors can also improve the *ME* coupling coefficient like:

1. Interfacial contact between electric and magnetic order parameter for better mechanical coupling.
2. Reduction of interfacial chemical reactions during sintering as they deteriorates Magneto electric coupling [28].
3. Processing technique, powders obtained via sol-gel method are fine as compared to solid state method. Which increases degree of freedom, interfacial contact and lattice strains that are important parameters for ME coefficient

Different type of lead- based and non-lead based multiferroic composites which are extensively studied as ME composites are shown in table1.

Table 1 Different kinds of lead- based and non-lead based multiferroic composites

Lead-based Multiferroic composites	Non-Lead based Multiferroic composites
1. Ba _{0.8} Pb _{0.2} TiO ₃ -Cu _{0.6} Co _{0.4} Fe ₂ O ₄ [29]	1. BaTiO ₃ -Ni _{0.92} Co _{0.03} Mn _{0.05} Fe ₂ O ₄ [38]
2. Pb _{0.2} Ba _{0.8} TiO ₃ - Ni _{0.75} Co _{0.25} Fe ₂ O ₄ [30]	2. KNN-LT-BNT-BT [39]
3. PZT – CFO [31]	3. CoFe ₂ O ₄ -BaTiO ₃ [40]
4. 0.68PZT- 0.32NiFe ₂ O ₄ [33]	4. BNT-BT-BAT [42]
5. Ba _{0.8} Pb _{0.2} TiO ₃ - Ni _{0.5} Co _{0.5} Fe ₂ O ₄ [35]	5. BNT-BT-YMNO [48]

1.4 Features of Multiferroic ME composites

- Ferroelectricity
- Piezoelectricity
- Magnetism
- Magnetostriction

Ferroelectricity:- Ferroelectricity in a material implies the occurrence of polarization that can be controlled and switched by the external applied electric field. When the electric field is applied, the electric dipoles of various regions called domains orient themselves according to the direction of field and makes large change in the polarization or dielectric constant value and on reversing the direction of field, dipoles switch from one direction of spontaneous polarization to another.

Piezoelectricity: - Piezoelectricity is the accumulated electric charge in certain materials that appear due to coupling between mechanical and electric properties. Electric voltage is produced when mechanical stress is applied, conversely, the applied voltage developed strains across the materials. These effects are called as direct and converse piezoelectric effects.

Ferromagnetism

Ferromagnetism takes place in the materials exhibiting spontaneous magnetization in the absence of magnetic field. To explain its physical phenomenon Pauli Exclusion Principle is used.

Magnetostriction:

When the magnetic field is applied on ferromagnetic/ferromagnetic materials, materials change its shape in the direction of an applied field known as Magnetostriction. The materials elongate or contract in the direction of applied field named as positive and negative Magnetostriction of material. The Magnetostriction coefficients of material is defined as the ration of change in length Δl to the original length l of the material i.e. ($\lambda = \Delta l/l$).

These characteristic features of *ME* coupled composites lies in its crystal structure as both ferroelectric perovskite and ferromagnetic spinel phase coexist in the *ME* composites which enhance their structural and magnetoelectric properties. In the next section we will briefly explain the perovskite as well as spinel structure of the material.

- **Perovskite oxides**

Perovskite basically belong to the family of oxide materials having general chemical formula ABO_3 where A is Bi^{3+} , Ba^{2+} and Pb^{2+} etc., and B is such as Fe^{3+} , Ti^{4+} , Zr^{4+} etc. BFO,

BNT, $BaTiO_3$ and $Pb(Zr,Ti)O$ are the examples of Perovskite materials, used as piezoelectric component for preparing of Multiferroic *ME* composites in bulk as well as thin film . Unit cell of such compounds is shown in **Fig.1. 2**

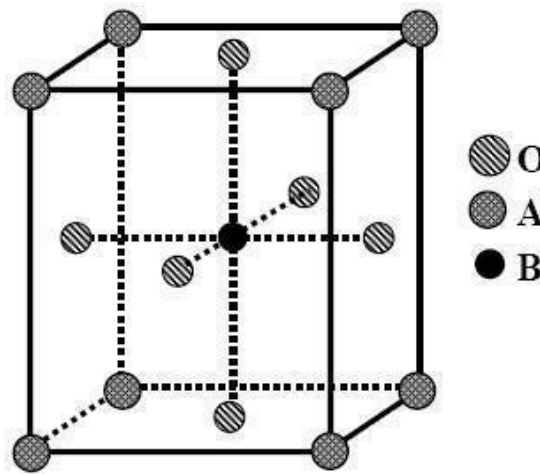


Fig. 1.2: Crystal structure of the Perovskite unit cell

- **Spinel ferrites**

Spinel ferrites are ferromagnetic metal oxides which are generally represented as AB_2O_4 , where A is divalent metal ion. For the preparation *ME* composites ferrites are used as ferromagnetic component. The crystal structure of Spinel ferrite is shown in **fig.1.3**.

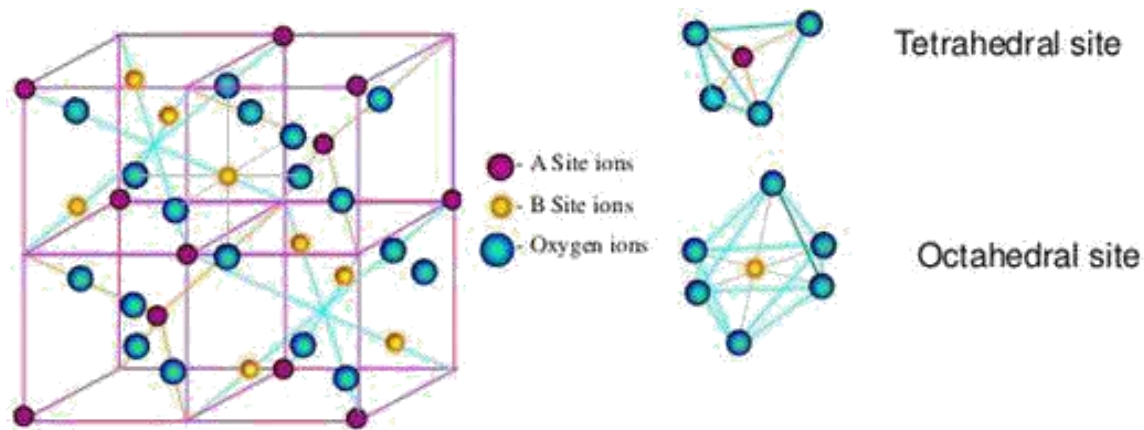


Fig. 1.3: crystal structure of the unit cell of Spinel ferrite

1.5 Applications of *ME* Coupled Composites:-

The Multiferroic composites have large and robust *ME* effect at room temperature which can be utilized for technical applications e.g. magnetic field sensor, transducer, filters, memory devices, phase shifters etc. *ME* composites can be used to design for magnetic field sensing devices. The Piezomagnetic component in *ME* composites responds to an applied magnetic field, which induces a electric charge in the piezoelectric component across the composite which makes it suitable for magnetic field sensor based applications. As both inductance and capacitance are present in a single component, the *ME* composites can also be used as LC filter which is an important application from the point of view of device miniaturization. The *ME* composites also can be used as phase shifter filter and transducers. *ME* composites have been suggested for biomedical applications such as wireless endoscopy, minimally invasive surgical tools, and stimulation of functions of living cells. The use of *ME* composites as a core material could be advantageous for tunable inductor applications since tuning magnetic properties by electric field is possible even at low fields. A variety of *ME* composite-based inductors have been made using different structures.

MOTIVATION

With the development of technology Magnetic materials has gained considerable attention due to their good ferromagnetic properties. These materials has been used for storage devices, such as hard disk drives, permanent magnets etc. and ferroelectric materials has been used for ferroelectric random access memories (FE-RAMs). Ferroelectric materials having good piezoelectric properties have been used for wide range of applications such as transducers and surface acoustic wave (SAW) devices. In recent few years more research took place on combining ferroelectric and ferromagnetic materials to form *ME* coupling composites. Still, researchers do lot of experiments by choosing different materials. As in literature, the composites having piezoelectric and magnetostrictive are mostly studied. More work is done on lead based ferroelectric oxides e.g. PZT for synthesis of *ME* composites but due to their toxic nature nowadays researchers paid more interest to Non-Lead based *ME* coupled

composites. $\text{Ba}(\text{ZrTi})\text{O}_3$ (BZT), BaTiO_3 (BT), BFO and BNT are main piezoelectric

materials which were used for preparing non lead based Magnetolectric composites.

Therefore, the main motive of the thesis is to investigate structural, dielectric, ferroelectric and magnetic properties of non-lead based magnetolectric composites. BNT-BT are chosen as ferroelectric and NZFO as ferromagnetic material for preparing ME composite.

CHAPTER II

LITERATURE REVIEW

Overview

A large amount of work has been carried out on Lead based *ME* composite, while meager data is available on Non-Lead based BNT-BT composites. This section summarize the important work carried out on lead base and non-lead base composites in last few years as *ME* coupled material.

The BNT based ferroelectric materials are mainly used for non-lead based magnetoelectric composites. BNT has been modified with different other solutions, to match the properties of PZT. However, High dielectric constant and piezoelectric coefficient of lead based ceramics makes them suitable for piezoelectric components for *ME* coupled composites. Therefore, to improve its ferroelectric properties, BNT has been modified with different solutions of BaTiO₃(BT), BKT, (K_{0.5}Na_{0.5})NbO₃ (KNN) and Bi(Mg_{0.5}Ti_{0.5})O₃ (BMgT). For the better performance of *ME* coupled composites, the magnetic components are selected on the basis of chemical stability, magnetostriction, permeability and resistivity. For this the Spinel ferrites (NFO, CFO) have been used because of high magnetostriction coefficient and good chemical stability. Hence, from past 10-15 years huge work was done on multiferroic composites, in which electrical and magnetic properties were identified.

Pb(Zr_{0.56}Ti_{0.44})O₃ – Ni_{0.6}Zn_{0.2}Cu_{0.2}Fe₂O₄, PZT-TDE composite, PZT-CFO, BiFeO₃-

CoFe₂O₄, Fe₃O₄/PbTiO₃, CoFe₂O₄/BaTiO₃, KNN-LT-BNT-BT are few examples of main *ME* composites which were reported earlier.

In 2002, M.B. Kothale et al. synthesized ME composites of $\text{Cu}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4 + \text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ by double ceramic sintering process. XRD patterns confirm the coexistence of both the phases. Temperature dependent dielectric studies were carried out in frequency range of 100Hz to 1 MHz. near the curie temperature, dielectric constant plots with respect to temperature give the broad maximum. There is an Magnetostriction effect produced in prepared composites due to applied magnetic field and Magnetoelectric conversion factor i.e dE/dH can be attributed to the strain

induced by lattice distortion in ferrites.[29] In the consecutive year, $(1-x)\text{Ni}_{0.75}\text{Co}_{0.25}\text{Fe}_2\text{O}_4 + x$ $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ ($x=0.0-1$) were prepared using ceramic method and the effect of two phases on ME coupling were analyzed. Variation of resistivity and thermo emf of the composites is studied. The maximum observed ME value was $140\text{Vcm}^{-1}\text{Oe}^{-1}$. Also temperature dependent dielectric

studies have been reported at different frequencies.[30]. In the same year cobalt ferrite/ PZT composites were fabricated to show that the ME effect is strongly affected by ac and dc magnetic field. The maximum obtained ME voltage coefficient 30.2 mV at 0.1T dc magnetic field and at 80 KHz ac frequency [31]. In 2004, work was done on the ferroelectric and piezoelectric to study the properties of the BNT-BT ceramics fabricated by the tape casting method. To obtain shape anisotropy in the particles OCAP and TGG method is used. As obtained textured BNT and BNT-BT ceramics showed larger piezoelectric properties as compared to non- textured ceramics composites [32]. In next year 2004, conventional ceramic method was used to prepare lead-

zirconate-titanate(PZT) and NiFe_2O_4 composite to measure ME coupling. The result showed that ME coupling strongly depend on volume fraction of NiFe_2O_4 , applied magnetic field and angle between polarization and magnetic field. the maximum obtained ME coefficient was $80\text{mVcm}^{-1}\text{Oe}^{-1}$ for the composition of $0.32\text{NiFe}_2\text{O}_4/0.68\text{PZT}$. Also, it was found that in ceramics, ME

response was linearly varied with ac and dc magnetic field [33].In 2005, the effect of microstructures on ME coefficients of multiferroic composites were studied. For this a self-consistent model was used for to analyse the effects of shape, and volume fraction, orientation distribution, of both phases on ME coupling. Theoretically and experimentally obtained results were compared and theoretical results are good agreement with experimental data[34]. In same

year , kadam et al. reported Dielectric studies and ME effect in $x\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3 + (1-$

$x)\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ composites($x=0, 0.55, 0.70, 0.85, 1.0$) which

were synthesized by double sintering method. XRD patterns confirmed the existence of single phases and both the phases in pure as well as composite multiferroic respectively. Temperature dependent dielectric studies i.e. dielectric constant and tangent loss was measured as a function of frequency. However, magnetoelectric conversion factor was studied as a function of applied magnetic field. The maximum obtained conversion factor was for $x=0.85$ and minimum for $x=0.55$ composites [35].

In 2006 Dae-Su Lee et al. reported Dielectric and ferroelectric properties of $(\text{Bi}_x\text{Na}_{0.5})\text{TiO}_3$ - BaTiO_3 ceramics. Hot pressing and templated grain growth methods were used to prepare the composites with different properties. For this SrTiO_3 was used as a template and $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - BaTiO_3 were used like matrix material. Better Piezoelectric coefficient(-79.6Pc/n) and electrochemical coefficient(0.35) were observed for the samples prepared by templated grain growth method as well as hot pressing method when compared to other specimens which are processed by solid reaction. These improved properties were due to the less pores in the matrix which are responsible for heterogeneous shrinkage and abnormal grain growth.[36]. **In 2007**, Bilayered composites thin films of PZT ceramics chip and terfenol-D/epoxy layers were investigated for the analysis of magnetoelectric resonance behavior. Bilayered composites films showed large capacitance as well as *ME* charge output. Three types of resonances were exist in the films i.e. first, second-order flexural also radial resonance respectively in each resonance frequency significance phase changes were observed. Higher flexural magnetic effect was obtained in thinner PZT chips. As-obtained bilayer structures showed large charge output of the order of 30Pc/Oe at resonance frequency. The Bilayered composite which have high magnetic field sensitivity has good applications in the sensors [37]. **In next year 2008**, ME composites

having Formula $(x) \text{BaTiO}_3 + (1-x) \text{Ni}_{0.92}\text{Co}_{0.03}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4$ with different series is prepared through double sintering ceramic process method. For the phase confirmation structural analysis has been done. Semiconductor behavior is observed by variation in resistivity. Dielectric behavior with different frequency ranges as been observed. Saturation magnetization (M_s) as well as coercivity (H_c) can be determined by using hysteresis measurements. The static magnetoelectric conversion factor (dE/dH) was measured as a function of dc magnetic field[38].**In same year** Yejing et al. reported electrical properties and phase transition behavior of KNN-LT-BNT-BT ceramics which were synthesized by conventional sintering method. Samples possess Perovskite phase

showed orthorhombic and tetragonal room temperature symmetries. These phase structures are formed because polymorphic phase transition temperature is decreased to room temperature. This paper shows the good properties but also indicates to relate this study with further need to promote the stabilities of ceramics so that they may utilize in varying

temperature environments [39]. **In next year** further work is reported on CoFe_2O_4 - BaTiO_3 nano composite powders and ceramics which were prepared by the molten-salt synthesis and sintering ceramic technique. Both Ferrite and ferroelectric phases were confirmed by the XRD technique. SEM images show appreciate perfect interface of both the phases. In the entire composites magnetic hysteresis loop shows good magnetic characteristics. These ME ceramics show good piezoelectric properties and magneto electric interaction between the ferromagnetic and ferroelectric phases [40]. **In same year** Tonshaku et al. prepared lead free BNT-BT-BNMN piezoelectric ceramic by conventional ceramic method. Single Perovskite phase is confirmed by XRD analysis. These ceramics show excellent piezoelectric properties when compared with hard PZT. These are used to fabricate a bolt-clamped Langevin transducer in ultrasonic cleanser. Ultrasonic cleansers having BNT's are more commercially used as compared to others [41]. **In next year**, BNT-BT-BAT ceramics were also reported by using conventional ceramic oxide method. Microstructure, piezoelectric and ferroelectric properties are discussed. There is no change in the crystal structure of BNT-BT with the addition of BAT composites but it changes the grain size of these ceramics more homogenous. With increase in y content the depolarization temperature of BNT-BT-BAT composite is decreased. In BNT-BT-BAT ceramics the polar as well as non-polar phases will coexist above depolarization temperature (T_d) [42].

In 2013, Sarir Uddin et al. reported mechanism of negative ECE effect of BNT-BT-BST single phased composites, which were prepared via sol gel method. By using thermodynamics Maxwell relations electro-caloric properties are investigated. As we seen in above research paper with the increase in BST content the depolarization temperature and dielectric constant temperature is decreased. Phase transitions of the composites of BNT-BT are affected when BST is doped. With the increase in doping content of the BST degree of unification was also increased. Overall result shows that BNT-BT-BST with negative ECE is promising content for refrigerants [43]. **In the same year** electrostrictive properties of the BNT-BT-KNN composites are investigated which were prepared by tape casting with pure BNT templates. It

is observed that the highly textured composites have good electrostrictive properties and highly thermal endurance. As compared to Pb based samples the composites having low electric field will possess a large electrostrictive response and the electrostrictive properties of these textured samples will little depend on the temperature range which will affect the practical applications of the textured samples [44] **In next year 2014**, piezoelectric properties of BNT-BT thin films are reported which are doped with Rb. These BNT-BT-Rbx thin films are deposited on Pt/Ti/SiO₂/Si substrate via MO deposition method. It is identified that with the Rb doping into BNT-BT thin films there is an enhancement in structural, morphological properties of BNT-BT thin films. Electrical properties with high dielectric constant polarization of thin films are observed with 5% Rb doping. These Rb doped BNT-BT thin films have preferably more used in future for piezoelectric devices and more potential for non volatile memories [45]. **In 2015**, Sixiang Ma et al. fabricates lead free BNT-BT-KNN piezoceramics via templated grain growth method. Electric-field induced strain of 91BNT–6BT–3KNN lead-free piezoceramics was reported. With high content of BNT templates results in composition variation from MPB of system disrupts the phases at zero electric field [46]. **In the same year** pyroelectric, dielectric and ferroelectric properties of the BNT-BT-ST is investigated. To create sintered samples 3BaO-3TiO₂-B₂O₃ glass was incorporated with different percentage composition. As a function of glass content hysteresis loop, coercivity, remnant polarization features are investigated. With the increase in the glass content depolarization temperature varies which shows the addition of glass content provides good temperature stability. Dielectric losses can also be decreased with the high glass content [47]. **In the same year**, microstructure and electrical properties of BNT-BT-YMNO have been reported. With the XRD analysis Perovskite phase is reported with no change in crystal structure. Clear grain boundaries are reported via scanning electron microscope. Hence, ferroelectric and piezoelectric properties can be increased with different x y content [48]. **In further year 2016**, Wei at al. reported the effect of stresses on piezoelectric properties of the BNT-BT-ST thin films which grown on different buffer layers. Electrical properties of thin films were greatly influenced by internal stresses which enhances the electrostrictive strain. Hence, by choosing different stress magnitudes, piezoelectric properties of these films can be adjusted [49]. Hence after this, high strain rate of BNT-BT-XBSn piezoelectric ceramics with different compositions were investigated which were prepared using conventional solid state

method. XRD Peaks shows the single Perovskite phase with no other secondary phase. *P-E* hysteresis loop showed the transitions from square to narrow slim loops which show NR AND ER relaxer behavior. With the end result it is verified that BNT-BT-XBSn is beneficial for generating large strain response which are great useful for actuator applications [50]. Aman Ulla et al. reported High strain response in ternary BNT-BT-BMnT solid solutions. Temperature dependent dielectric and ferroelectric properties are investigated. With the addition of BMnT there is disruption in the ferroelectric behavior [51]. Further Dielectric relaxation and electric conduction behavior is investigated by preparing $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-BaTiO}_3)\text{-xNaNbO}_3$ ((BNT-BT)-NN) ceramics. The bulk conductivity patterns shows the electronic conduction which was confirmed by Arrhenius law with having $E_a = 1.24\text{--}1.55$ eV. For the conduction process, the electronic conduction ceramics were assumed to be responsible. With the increasing content of NN the freezing and burning temperatures were calculated [52]. **In next year 2017**, $0.93\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.07\text{BaTiO}_3$ (BNTBT) and KNbO_3 (KN) powders were prepared by sol-gel and hydrothermal method with average size of particles is ~ 50 nm and ~ 300 nm respectively. Then, $(1-x)(\text{BNTBT})\text{-xKN}$ (BNTBT-KN, $x = 0, 0.01, 0.03, 0.05, 0.07$) composites were prepared in $x = 0, 0.01, 0.03, 0.05, 0.07$ weight fraction by using these powder precursors. Their structural, energy-storage as well as dielectric properties were investigated. All the composites showed single Perovskite structure, indicating the homogeneous mixing of KN into BNTBT. High dielectric constant was observed for BNTBT-KN Multiferroic ceramics at room temperature, within range of 1430–1550. With the increase of KN content the Ferroelectric loops formed at room temperature becomes slimmer, which highly improves energy-storage density as well as efficiency. All the results shows that $0.95\text{BNTBT}\text{-}0.05\text{KN}$ synthesized by wet-chemical method is a good lead-free dielectric material for the energy-storage capacitors [53]. Ying chen et al. reported LiNbO_3 -doped $0.94(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3)$ (BNT-BT) ceramics were prepared to investigate ferroelectricity and electric field-induced strain. A large strain of 0.6% (at 70 kV/cm) was obtained in the 2.5%- LiNbO_3 -doped BNT-BT at room temperature which was higher than $\text{Pb}(\text{Zr,Ti})\text{O}_3$. The obtained piezoelectric coefficient was 857 pm/V, which is high among the BNT-based ceramics. The maximum normalized strain 950pm/V at 74°C suggests that mixed ferroelectric rhombohedral and relaxor tetragonal phase was responsible for large electromechanical response [54]. ME composite of $(x) \text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}(1-x) \text{MgFe}_2\text{O}_4$, with

x=0, 0.5, 0.6, 0.7, 0.8 and 1.0 were reported by solid state reaction method. The composites were found to exhibit mixed spinel-Rhombohedral phase. With the addition of BNT content, Average grain size increased from 0.62 to 2.90 μm . Temperature dependent dielectric studies showed anomalous behavior at T_d , which is due to the transition of BNT from ferroelectric to antiferroelectric. *ME* coupling coefficient also increased to 4.793 mV/cm-Oe for x=0.8 in composites. The applied magnetic field induced strain in the composites which changes the position of ions and resulting the induced voltage. Results showed that BNT is a potential candidate for lead-free *ME* composites [55]. **In same year**, Lead-free piezoelectric

composites $0.9\text{BaTiO}_3-(0.1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x\text{BiMO}_3$, where, M=Al and Ga (x=0.00-0.10), were synthesized by solid-state reaction technique. Results showed that BiMO_3 significantly affect electrical properties as well as phase transition of the BT-BNT ceramics.

The addition of BiAlO_3 made no changes was observed in T_m by the addition of BiAlO_3 , however, a small change in ferroelectric and piezoelectric properties of xBA ceramics were observed. Gradual decrease in Pr, T_m , d_{33} and EC were observed with BiGaO_3 content, which is due to disruption in ferroelectric state by Ga^{3+} substitution [56].

CHAPTER III

EXPERIMENTAL PROCEDURE AND CHARACTERIZATION TECHNIQUES

Overview

Various synthesis processes are used for making powders like solid state method, hydrothermal method etc. Our synthesis process is Sol gel method. After preparing separate powders of BNT-BT and NZFO they were mixed by using Ball Mill. This chapter provides detailed information of synthesizing the samples of different compositions. The flow chart of BNT-BT-NZFO synthesis is also added.

Sample preparation:

The sample preparation section is divided in three sections i.e. preparation of BNT-BT, NZFO and (1-x) BNT-BT-(x) NZFO composites.

High purity bismuth Nitrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$], Sodium Nitrate [$\text{Na}(\text{NO}_3)$], Titanium isopropoxide [$\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$], Barium Nitrate [$\text{Ba}(\text{NO}_3)_2$], Nickel Nitrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], Zinc Nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], Ferric Nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], Acetyl Acetone [$\text{CH}_3\text{COCH}_2\text{COCH}_3$], Propionic acid [$\text{C}_3\text{H}_6\text{O}_2$], 2-Methoxyethanol [$\text{C}_3\text{H}_8\text{O}_2$] of Sigma Aldrich (99.99%) were used for the synthesis. BNT-BT and NZFO samples were prepared by sol-gel method.

- **Synthesis of pure BNT-BT:** To prepare BNT and BT powders, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Na}(\text{NO}_3)$, $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ were dissolved into 2-Methoxyethanol and $\text{Ba}(\text{NO}_3)_2$ and $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ were dissolved in propionic acid. As obtained solutions BNT and BT were mixed and stirred for 6 hours to obtain homogeneous mixture. Mixture was heated 70°C until powder is formed. The as obtained dried powder was calcined at 850°C for 3 hour in resistance furnace.

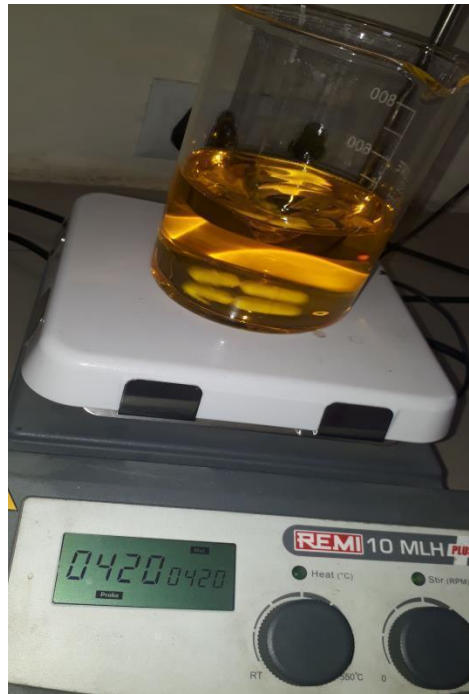


Fig. 3.1 Sol formation using magnetic stirrer

- **Synthesis of pure NZFO:** To prepare NZFO, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in deionized water and stirred for 4 hours. A pH of ~ 7 was maintained by adding NH_3 solution during stirring. The solution was heated at $70\text{-}80\text{ }^\circ\text{C}$ to turn into viscous gel. This gel was ignited in air resulting in the formation of black color powder. The powder was calcined at $900\text{ }^\circ\text{C}$ for 3 hour in resistive furnace shown in fig.3.2



Fig 3.2 Resistive furnace

- **Synthesis of (1-x) BNT-BT-(x) NZFO Composites:** Selected compositions of BNT-BT-NZFO composites as shown below were prepared from BNT-BT and NZFO powders.



0.95(BNT-BT) - 0.05(NZFO)



0.90(BNT-BT) - 0.10 (NZFO)



➤ 0.85(BNT-BT) - 0.15(NZFO)

➤ 0.80(BNT-BT) - 0.20(NZFO)

0.75(BNT-BT) - 0.25(NZFO)



0.70(BNT-BT) - 0.30(NZFO)

The desired compositions were physically mixed and wet milled in a planetary ball mill (shown in fig) for one hour. As milled powders were dried and pressed into pellets using hydraulic press under pressure of 10 MPa and sintered at 1000 °C for 1h in ambient atmosphere.



Fig. 3.3 Ball mill

The methodology used for the synthesis of BNT-BT-NZFO composites using sol-gel technique is shown with the help of fig.3.1 and flow chart 1.

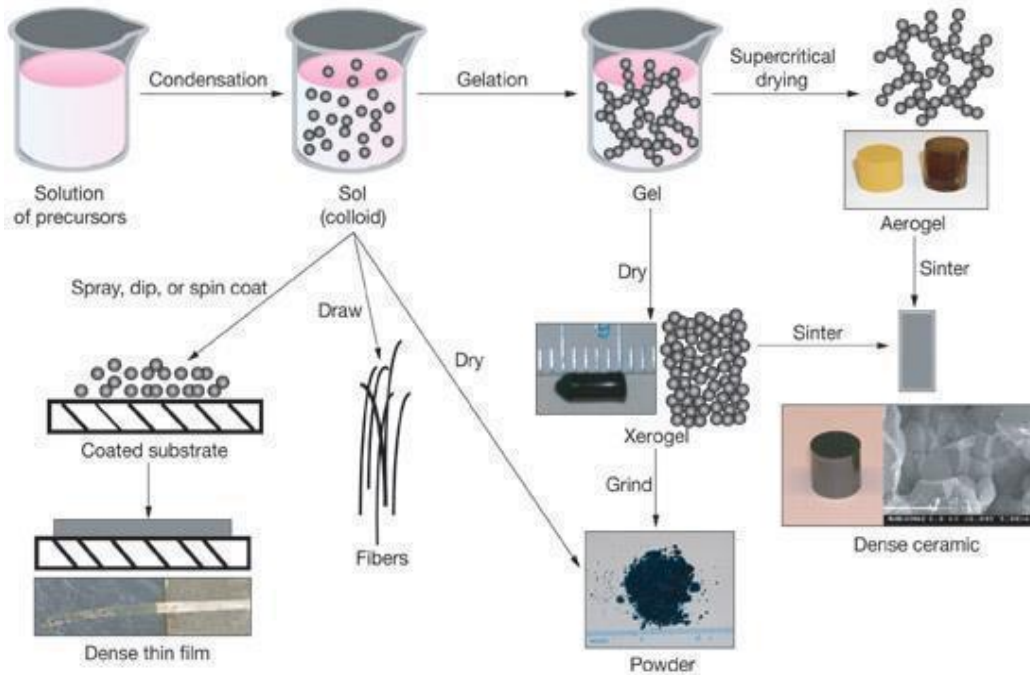
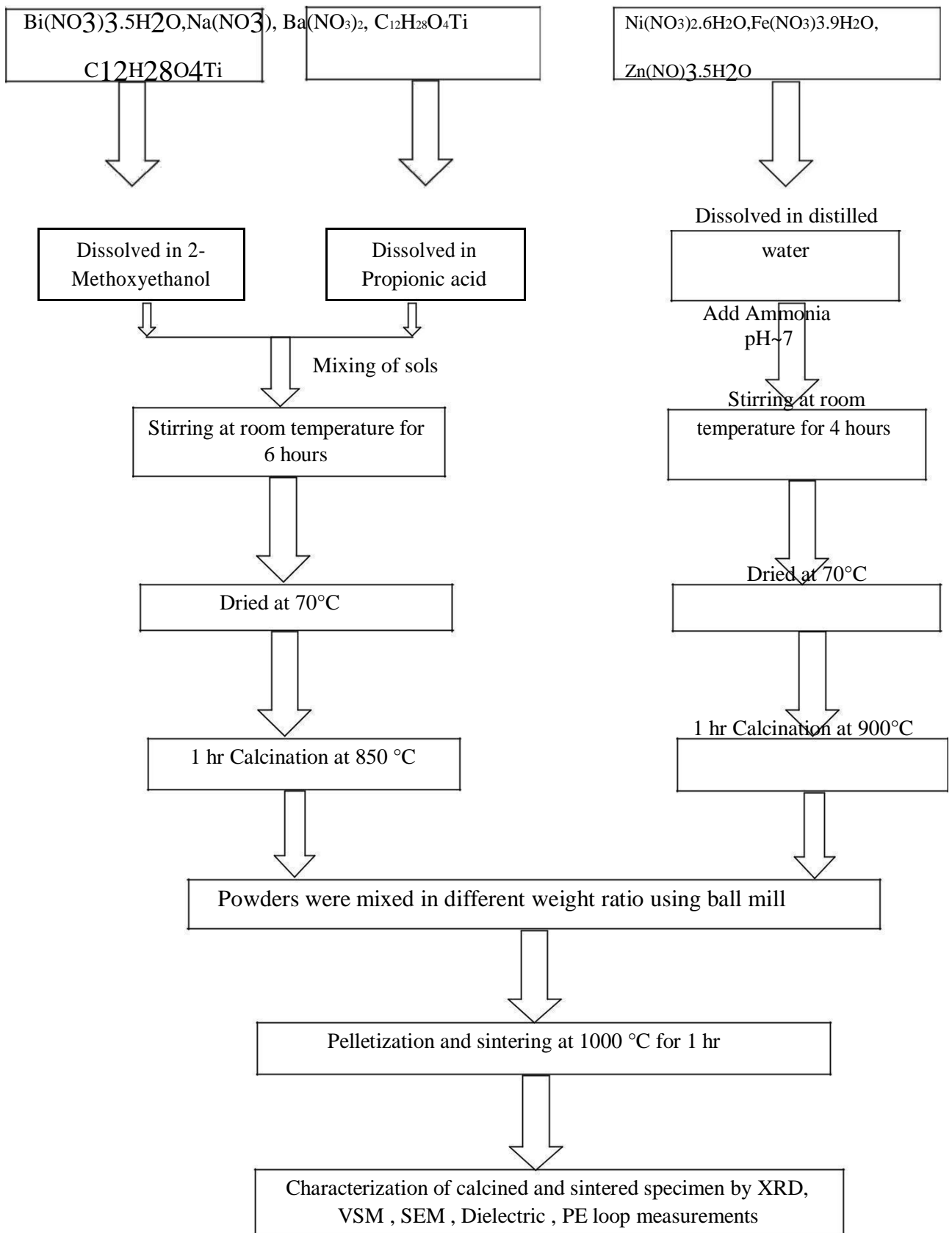


Fig. 3.4 Preparation of samples via Sol-gel technique



Flow Chart 3.1 Flow chart of synthesis of *ME* composites

1.2 Characterization techniques

Phase and microstructural characterization were carried out by X-ray diffractometer (XRD) and scanning electron microscopy (SEM) respectively.

Magnetic, dielectric and ferroelectric measurements of BNT-BT-NZFO composites were analyzed by, vibrating sample magnetometer (VSM), impedance analyzer and PE loop tracer.

X-ray diffraction (X'PERT Pro-Panalytical using Cu-K α radiation wavelength (1.5405 Å)) has been used to analyze phase formation. values vary from 20 to 80°.

Scanning electron microscope (SEM) is used to study the surface morphology using the model of JEOL (JSM-IT100).

Vibrating sample magnetometer (VSM) was used to study the magnetic properties of the BaM thin films. Model of the VSM used is lake shore 7404. Magnetization field for both powder and thin film was applied from -10000 to 10000 Oe. From the hysteresis loop we measure the

M_S , M_r and H_C of the composites.

High temperature dielectric measurements of the sintered pellets were performed using impedance analyzer Solartron – SI 1260.

Polarization (P - E) electric field hysteresis loops for all samples were performed at room temperature using the ferroelectric tester (Radiant technologies Precision Premier (II)).

Chapter IV

RESULTS AND DISCUSSION

Overview

Sol-gel assisted BNT-BT-NZFO magnetoelectric (*ME*) composites have been synthesized. The effect of addition of ferrites on structural, ferroelectric, magnetic and dielectric properties has been studied systematically. In this section obtained results of these composites are reported and discussed.

4.1 XRD Analysis

Fig. 4.1 shows the X-ray diffraction patterns of pure BNT-BT, NZFO and BNT-BT-NZFO composite samples prepared by sol-gel method. In pure BNT-BT and NZFO samples, all the diffraction peaks corresponds to single phase without any secondary phase. XRD patterns of BNT-BT-NZFO composites confirm the co-existence of both the perovskite and spinel phases. However, peak of BNT-BT-NZFO (32.51°) has been shifted towards the higher angle (32.71°). This shifting is due to interfacial stresses developed between the BNT-BT and NZFO phases. The lattice parameters and crystallite size for all pure and composite samples were calculated using Scherer relation as follows.

$$\tau = \frac{K\lambda}{\beta \sin \theta}$$

Where, τ is crystallite size, K is dimensionless shape factor, λ is a wavelength, β is full width half maxima (FWHM) and θ is Bragg's angle. The observed crystallite size of pure BNT-BT and NZFO was $280.06\mu\text{m}$ and $352.29\mu\text{m}$ respectively and average crystallite size of 70-30 composite was $327.85\mu\text{m}$.

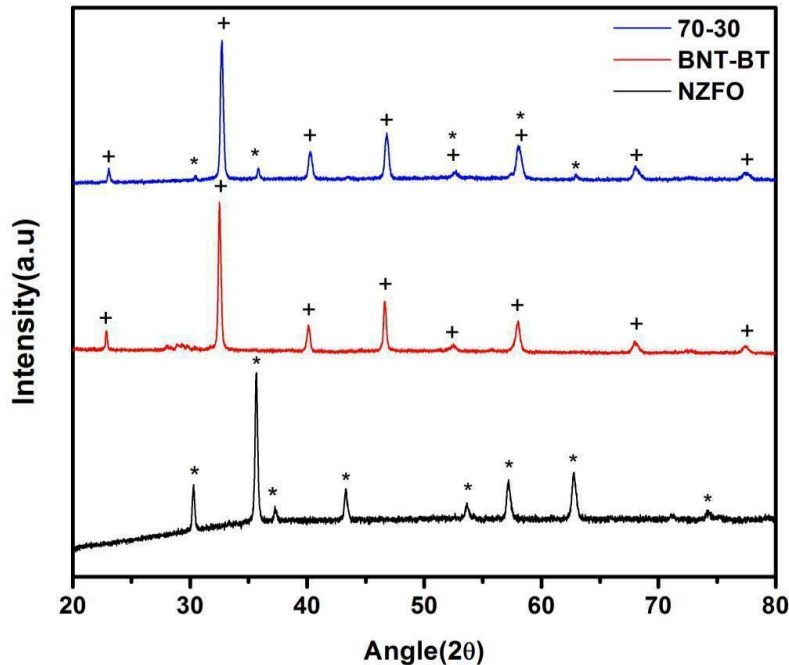


Fig.4.1 XRD patterns of pure NZFO, BNT-BT and $(1-x)[0.95(\text{BNT})-0.05(\text{BT})] - x\text{NZFO}$ ($x=0.3$) ME composite.

4.2 Surface morphology (SEM)

Fig. 4.2 (a,b) shows the SEM micrographs of fractured surface of pure BNT-BT and BNT-BT-NZFO composite sample ($x = 0.30$) which were sintered at 1000°C . The pure BNT-BT sample shows larger grains as compared to the composite samples. With the addition of NZFO there is a reduction of grain size. The reduction in grain size could be the result of pinning action of NZFO in the composite.

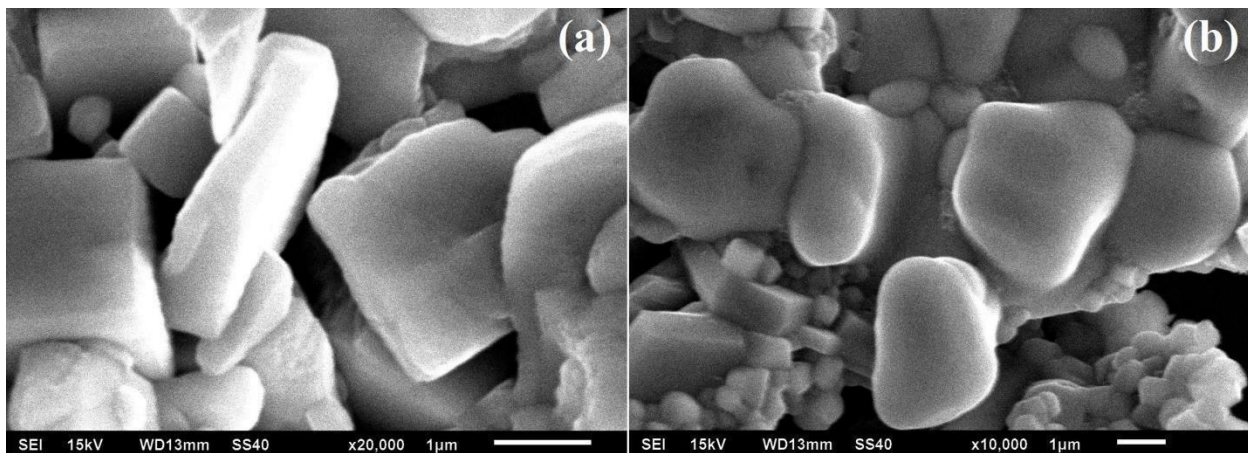


Fig.4.2. SEM images of (a),(b) $(1-x)[0.95\text{BNT}-0.05\text{BT}]-x\text{NZFO}$ ($x=0, 0.30$) *ME* composite

4.3 Magnetic Measurements (VSM):

Fig.4.3 Shows the $M-H$ loops of $(1-x)\text{BNT-BT}-x\text{NZFO}$ composite ($x = 0.05-0.30$). The well saturated $M-H$ loop indicates the ferromagnetic nature of the composite. The magnetization increases with the increase of ferrite content. The highest values of M_S and M_r for composites ($x = 0.30$) found to be ~ 19.78 emu/g, ~ 2.14 emu/g respectively. The coercive field is so small due to soft ferrite behavior of the NZFO.

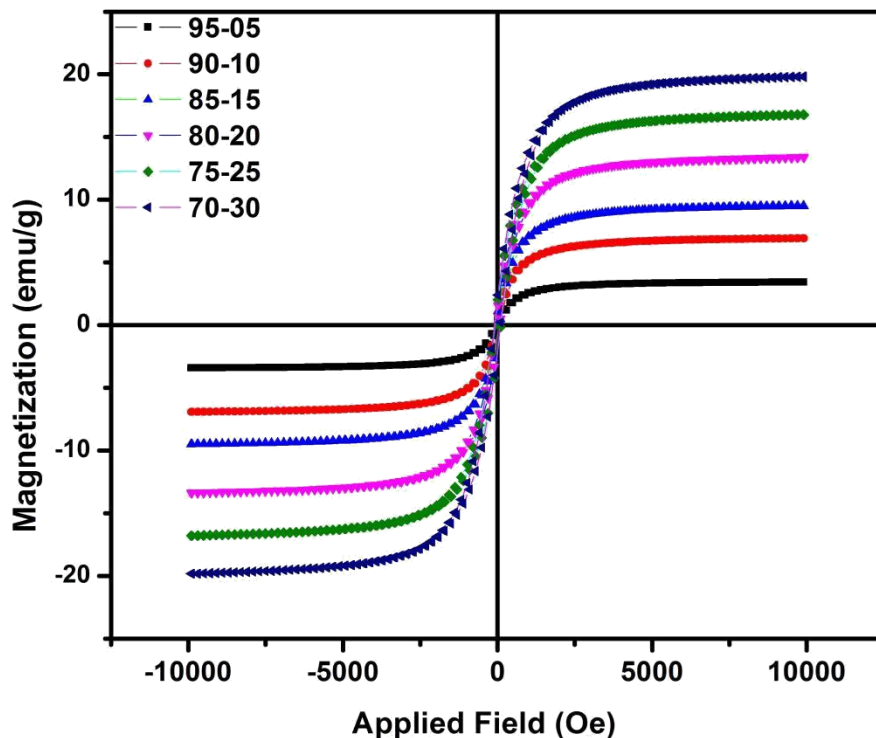


Fig.4.3 *M-H* loops of(1-x) BNT-BT-(x)NZFO *ME* composites

4.4 Dielectric studies:

Fig.4.4 (a-b) shows the temperature dependent dielectric behavior of $(1-x)[\text{BNT-BT}]-x$ NZFO composites where $(x=0,0.1,0.15,0.25,0.3)$ measured at 1 kHz. The dielectric constant (ϵ') (fig.4.4 a) for all samples continuously increases with temperature. However, As compared to pure BNT-BT, composite shows steep increase. The dielectric loss (ϵ'') (fig. (4b)) decreases with temperature for pure BNT-BT and increase for composites. However, particularly at higher temperature the abrupt increase in ϵ' and may due to the increase in conductivity with temperature which may increases the drift mobility of thermally activated charge carriers. This behavior can be interpreted through the hopping conduction mechanism of charge carriers between tetrahedral and octahedral sites. This electron exchange mechanism between $(\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+})$ as well as $(\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+})$ causes exchange polarization and therefore enhance the total polarization.

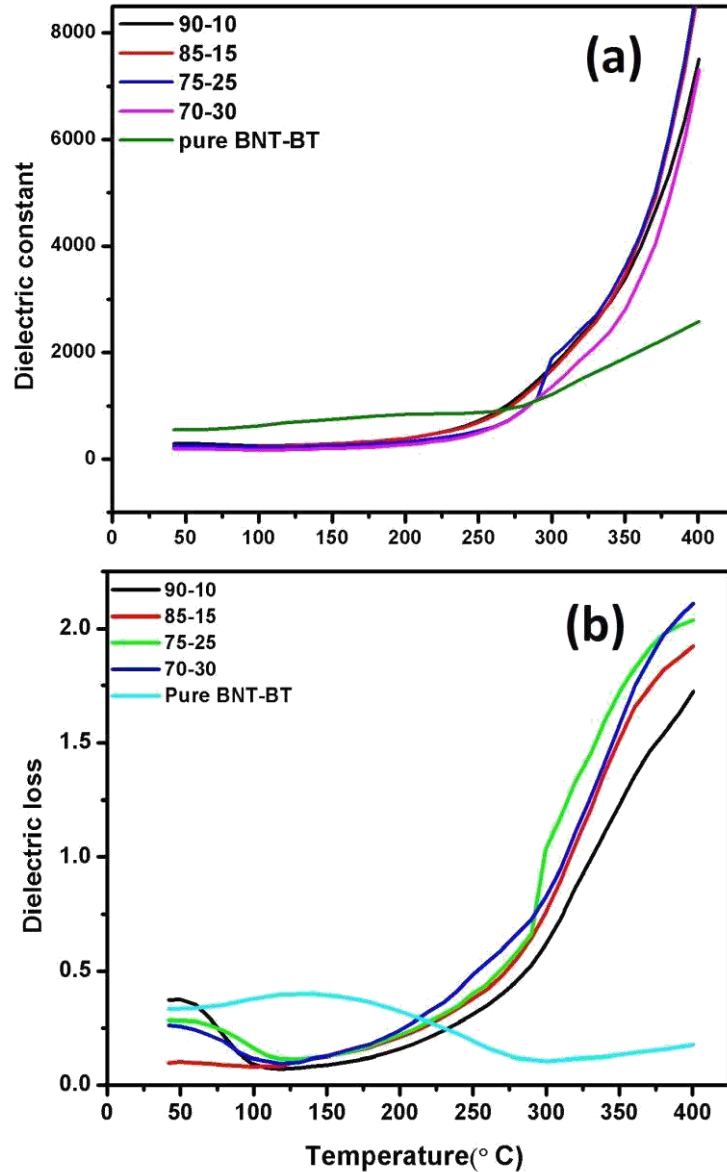


Fig. 4.4 (a-b) The temperature dependent dielectric constant (ϵ') and dielectric loss of $(1-x)\text{BNT-BT}-(x)\text{NZFO}$ ($x=0,0.1,0.15,0.25,0.3$) *ME* composite at 1kHz frequency.

4.5 Ferroelectric measurements

Fig.4.5 shows the *P-E* loops of pure BNT-BT and composite samples, which were measured at 1 Hz frequency. Pure sample ($x=0.0$) shows proper saturated hysteresis loop with large

remnant polarization ($23.2 \mu\text{C}/\text{cm}^2$). The P_r for composite samples decreases continuously with increase in NZFO content. Also the dominant lossy behavior composite sample can be

attributed to higher content of NZFO, which lead to increase in conductivity of composite. Such type of lossy P - E loops are often observed in samples with higher conductivity and are often named as non-ferroelectric P - E loops

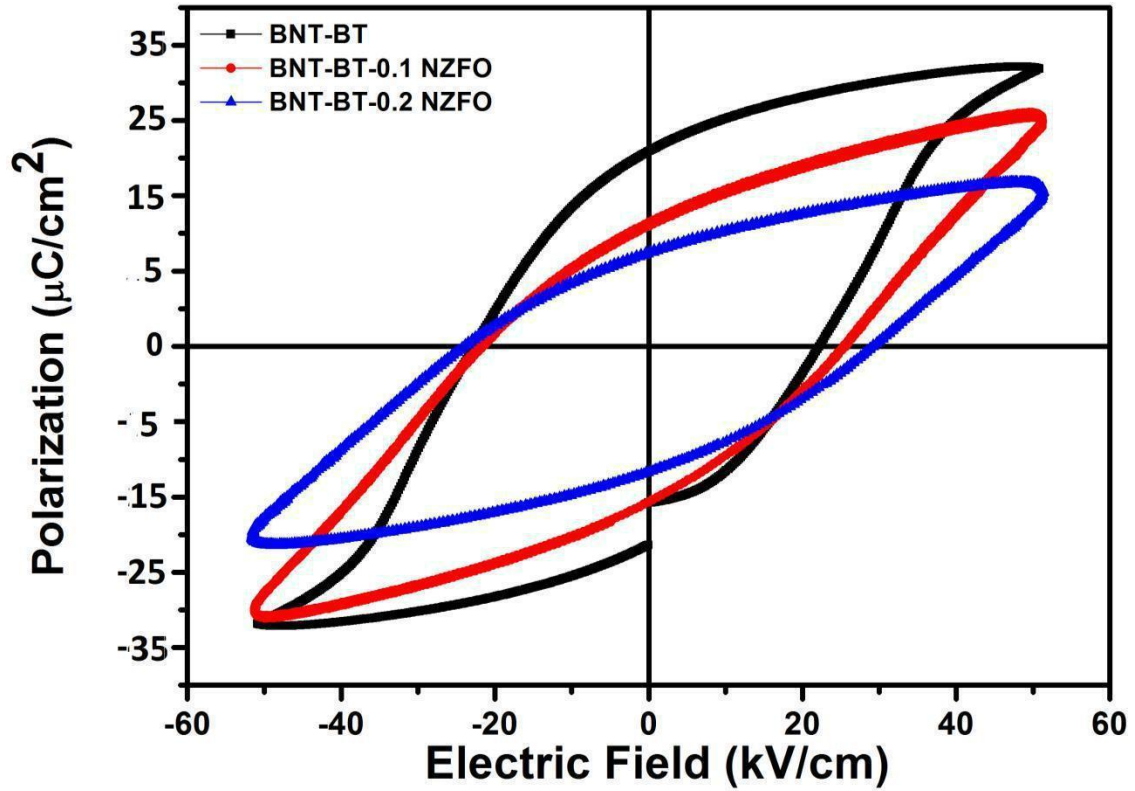


Fig. 4.5 P - E loops of $(1-x)\text{BNT-BT}-x\text{NZFO}$ ($x=0.0, 0.1, 0.2$) ME composites.

Conclusion:

Lead free *ME* particulate composite series $(1-x)[0.95(\text{BNT})-0.05(\text{BT})] - \text{NZFO}$ ($x = 0.05, 0.10, 0.15, 0.20, 0.25, 0.30$) was synthesized successfully using sol-gel method. Further, structural, magnetic, ferroelectric and dielectric properties were studied. XRD patterns of BNT-BT-NZFO composites confirm the co-existence of both the perovskite and spinel phases. SEM micrograph shows the well distinguished grains in pure as well as in composite. With the addition of NZFO there is a reduction of grain size. Temperature dependent Dielectric measurements indicate that dielectric constant consistently increases whereas dielectric loss decreases in pure BNT-BT.

Ferroelectric measurement shows that remnant polarization (P_r) decreases with the addition of NZFO content.

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