OPTIMIZATION OF FUNCTIONAL PROPERTIES OF

LEAD-FREE BiFeO₃-BaTiO₃

M.Tech. Thesis

By SIDDHANT SHARMA



DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIAL SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE

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OPTIMIZATION OF FUNCTIONAL PROPERTIES OF LEAD-FREE BiFeO3-BaTiO3

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Technology

> by SIDDHANT SHARMA



DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIAL SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis OPTIMIZATION OF FUNCTIONAL PROPERTIES OF LEAD-FREE BiFeO3-BaTiO3in the partial fulfillment of the requirements for the award of the degree of MASTER OF TECHNOLOGY and submitted in the DISCIPLINE OF METALLURGICAL ENGINEERING AND MATERIAL SCIENCE, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from August 2021 to May 2023 under the supervision of Dr. Rupesh S. Devan and Dr. Ravindra Jangir.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Irma

(SIDDHANT SHARMA)

This is to certify that the above statement made by the candidate is correct to the best of my/our

knowledge Supervisor

Dr. Rupesh S. Devan

External Supervisor Dr. Ravindra Jangir

SIDDHANT SHARMA has successfully given his M.Tech. Oral Examination held on 25 May 2023.

Signature(s) of Supervisor(s) of M.Tech. thesis Date: 12/06/23

Signature of PSPC Member 1 Date: 12.06.23

(Acting DPGC) Convener, DPGC Date: 13/06/2023

P. Aur Bri Signature of PSPC Member 2 12/06/ 2023 Date:

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Abstract

In the present work, the optimization of synthesis conditions of lead-free (1-x)BiFeO₃-xBaTiO₃ (x being the mol fraction) solid solution is conducted to improve its functional properties. Two common routes to prepare this solid solution are given in the literature. In the first route, precursor oxides of Barium (BaCO₃), Titanium (TiO₂), Bismuth (Bi₂O₃) and Iron (Fe₂O₃) are mixed together and heat treated. While in the second route, Barium Titanate (BaTiO₃) is used as a precursor and mixed with the Bismuth and Iron oxide and then heat treated. For this work, the second method was taken into consideration, which led to the synthesis of two BaTiO₃ samples. These samples underwent a calcination process for 10 hours and 18 hours, respectively. Quantity of excess Bi₂O₃ is also added from 0 to 2 mol % while preparing solid solution samples to compensate for the bismuth volatilization effect. This led to the synthesis of five different samples. These samples were structurally characterized using synchrotron-based X-Ray Diffraction, which showed no signs of secondary phases, and the Le Bail fitting of XRD data proved the existence of Pm-3m and R3c phases together. Morphological characterization of these samples was done using field emission scanning electron microscopy, which revealed bimodal grains with grain boundaries. These two characterizations did not reveal any significant difference among these five samples. However, when electrical measurements were done, the (1x)BF-xBT sample, which had been prepared using BaTiO₃ for a shorter calcination period of 10 hours and had 1% excess Bi₂O₃ in it showed the highest dielectric constant of 32000 at 10kHz frequency and had lowest dielectric loss as well among five samples. Polarization- Electric Field loops showed similar results for this sample and exhibited typical ferroelectric response with remnant polarization of 32 MC/cm², the coercive field of 30 kV/cm, and saturated polarization of 40 MC/cm². Considering the superiority of this sample, electrochemical measurements were done where cyclic voltammetry results showed a specific capacitance

of 173 F/g at 5mV/s scan rate with a discharge time of 40 seconds at 1A/g in Galvanostatic charge discharge cycles. These results prove that when solid solutions of BiFeO₃-BaTiO₃ are prepared using a solid-state reaction route, the calcination time of BaTiO₃ chosen here as a precursor is crucial in optimizing the functional properties. Hence to prepare the solid solution of (1-x)BF-xBT, the BaTiO₃ chosen must be calcined for the shorter duration instead of longer ones, and 1 mol % excess Bi₂O₃ is sufficient to overcome the bismuth volatilization effect. These conditions would lead to the synthesis of lead-free BiFeO₃-BaTiO₃ with better functional properties.

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NOMENCLATURE

BTO (01)_LT: Barium Titanate calcined for 10 hours

BTO (01)_MT: Barium Titanate calcined for 18 hours

BFBT33: 0.67BaTiO₃-BiFeO₃ Solid Solution

BFBT33_03: BFBT solid solution containing BTO (01) $_$ LT + Bi₂O₃ : Fe₂O₃ (1:1)

BFBT33_04: BFBT solid solution containing BTO (01) _ LT + Bi₂O₃ : Fe₂O₃ (1.01:1)

BFBT33_12: BFBT solid solution containing BTO (01) $_{\rm MT}$ + Bi₂O₃ : Fe₂O₃ (1.01:1)

BFBT33_14: BFBT solid solution containing BTO (01) $_LT + Bi_2O_3$: Fe₂O₃ (1.02:1)

BFBT33_16: BFBT solid solution containing BTO (01) $_{\rm MT}$ + Bi₂O₃ : Fe₂O₃ (1.02:1)

Pr: Remnant Polarization

Ec: Coercive Field

Pmax: Maximum Polarization

ε_r: Relative permittivity

E': Permittivity real part

ε["]: Permittivity imaginary part

Eo: Permittivity of free space

tan δ : loss tangent

P: Polarization

D: Di-electric displacement

Z': impedance real part

Z'': impedance imaginary part

M': modulus real part

M'': modulus imaginary part

E_a: activation energy

T: Temperature (in Kelvin)

f: frequency (in Hertz)

i_p: Peak current

v: Scan rate

Cs: Specific capacitance

C: Specific capacity

V: Potential at working electrode vs. reference electrode

d_{hkl}: Interplanar spacing on (hkl) plane

i: Current

m: Mass of active material

E: Potential window in which potential is swept

 Δt : Discharge time in GCD

N: Number of electrons involved in the corrosion reaction

F: Faraday's constant

Rs: Solution resistance

RCT: Charge transfer resistance

Q: Constant phase element

W: Warburg's impedance

ACRONYMS

FESEM Field effect scanning electron microscope.
XRD X-ray diffraction.
EIS Electrochemical Impedance Spectroscopy.
EDLC Electric double-layer capacitance.
SA Surface area of the sample.
CSA Cross-sectional area of the adsorbate.
SCE Saturated Calomel Electrode.
NiS/NiF Nickel sulfide on Nickel foam.

Chapter 1

Introduction

1.1 Foreword

Since the dawn of civilization, humans have continuously explored the true nature of their surroundings. Whether it be harnessing the power of combustion and putting it to use in automotive or creating chemical gradients in systems that cause electrical flow as seen in batteries. Our modern-day technology heavily relies on electronics. Whether it be a system of computation involving data storage and its processing or complex electrical circuits used in automation. The use of actuators and sensors is quite common in energy harvesting and signal-relaying devices. Actuators are used in industrial machinery for precise position control of valves, in probes of Scanning Tunneling Microscope and Atomic Force Microscopy [1], and in charge coupled device where pixel deviation technique is used to acquire an image with better resolution overcoming effect of hand blurring. The principle exploited here is the piezoelectric effect, in which when a material is under the influence of mechanical stress, its internal structure tends to form charged dipoles whose response can be registered in terms of surface charge, and the converse of this effect also holds true. This discovery made by the Curie brothers in 1880 also finds its use in sensors today. Pressure measurement in fluids or explosives, snap action relay, temperature, acceleration and strain measurement could also not be executed without sensors. The cause of piezoelectricity lies in the non-centrosymmetric geometry of the unit cell, which also leads to another important property of ferroelectricity in polar materials where there already is remnant polarization of charged dipoles and further polarization could be achieved under the presence of the electric field. After the discovery of ferroelectrics in 1920 by Valasek, they became a topic of interest, and nowadays, they find their use in capacitors, field effect transistors, and

ferroelectric random-access memory (FeRAM) [2]. Ferroelectrics also find their use in optoelectronic applications, such as in solar cells, where the presence of an internal field gives better carrier charge dynamics. Also, it is used in heterojunction devices where the remnant charge dipole density makes the heterojunction behave like a P-N diode.

The class of materials that constitutes the non-Centro symmetry required and variety of tunability in terms of their band tuning and strain incurred are perovskites; some ferroelectric perovskites are known to have high curie temperatures and can be used for high-temperature piezoelectric applications as in fuel modulation, deep oil drilling and wind turbines. Perovskite oxides have the generic formula of ABO₃. Here A site atoms are in twelve-fold coordination and are occupied by alkali metal ions, whereas transition metal ions occupy B site and are in six-fold coordination.



Fig. 1.1: a.) Strategies to improve perovskite oxide structure for various applications, b.) Basic perovskite structure with the green atom as A site, red one as oxygen atoms, and white one as B site.

Both A and B site elements are cations and comprise +6 charge on them and three oxygen ions having -6 charge making a unit cell charge neutral. Here site A can have an ion with a +1, +2 and +3 oxidation state, and site B can have an ion with a +3, +4 and +5 oxidation state. As doping strategies and various possibilities of combination of compounds can be formed in perovskites, a geometric factor known as tolerance factor proposed by Goldschmidt in the 1920s is the determining factor for the stability of the structure and especially the distortion associated with the BO₆ octahedra. The tolerance factor is given as follows:

$$t = (r_a + r_o)/\sqrt{2}(r_b + r_o)$$

Here r is the radius of atoms, 'a' denotes atoms at the A site, and 'b' denotes atoms at the B site, respectively. The value of this tolerance factor should ideally be one, and any deviation from this signifies distortion in BO_6 octahedra and deviation from cubic symmetry. If 't' is more than one, the system moves towards tetragonal or hexagonal symmetry, and if 't' is less than one, then monoclinic, rhombohedral, or orthogonal symmetry would be observed.

When ferroelectricity was discovered in perovskite oxides in the 1940s, it came with a high dielectric constant, making them a necessary candidate for multilayer ceramic capacitors. Another important feature of ferroelectric perovskite is its phase transition at a certain temperature called curie point (T_C) , around which it transits from a paraelectric phase to a ferroelectric phase. This combined with the possibility of forming solid solutions such as between BaTiO₃ and SrTiO₃ where the curie temperatures are 400K and 105K, respectively, allowed the curie temperature to be around room temperature where we can exploit high dielectric constant. Hence after considering characteristics packed in ferroelectric perovskite [3] oxides, it became evident that their properties should be explored to better understand structural and functional properties and the effect of synthesis conditions on them. The system considered in this study is a solid solution of Bismuth Ferrite and Barium Titanate. The reason to choose this material is to have the comfort of both high T_C due to BiFeO₃, which is also a good multiferroic showing both ferroelectric and magnetic ordering, and BaTiO₃, which is polar dielectric shows good ferroelectric and

piezoelectric properties. This overcomes the shortcoming observed in the lead titanate system (PbTiO₃) with $T_C=490^{\circ}C$ and health hazards observed due to the use of lead. Another reason for studying lead-free ceramics is the high density of PZT (7.8g/cm³). In the further section, we will consider each material individually and then its solid solution and literature review.

1.2 Introduction to BiFeO₃

Since the discovery of BiFeO₃ in 1957, it was realized as a single-phase multiferroic material, and researchers started digging into its ferroelectric, dielectric, magnetoelectric and piezoelectric properties, and now also photovoltaic properties due to its band gap ranging between 2.2 to 2.4eV which falls under the visible spectrum. Various studies on this material showed that remnant polarization could exceed the value of about 150μ C/cm² [4] in thin films due to the effect of lattice strain. Researchers have also studied the mechanism of leakage current and optimized synthesis methods for producing highly insulating samples having functional properties such as d₃₃ value (>50pc/N) and T_C(>700°C) [5]. In subsequent sections, we have discussed the crystal structure and processing methods of the material considered.

1.2.1 Crystal Structure

BiFeO₃ has a rhombohedral crystal structure with R3c space group where "R" stands for rhombohedral geometry, 3 stands for the fact that one hexagonal unit cell has 3 lattice points, and "c" stands for the fact that the hexagonal unit cell has a point symmetry. The reason for ferroelectricity in this material is due to two distortions, one being polar displacements of anion and cation cages respective to each other being the rotation of FeO₆ octahedra along [111] direction in rhombohedral geometry [6].



Fig 1.2: BiFeO₃ structure shown with rotation of FeO₆ [7].

Both Bi and Fe in this material are in +3 oxidation state. The method considered to synthesize BiFeO₃ is solid state reaction where proper mixing of Bi₂O₃ and Fe₂O₃ using milling is to be done, and after that, high-temperature calcination is to be conducted to execute interdiffusion of cations; the kinetics of such a reaction is slow, and hence powder particle size is important. A few intermediate phases are formed, such as Bi₂Fe₄O₉, Bi₂₅FeO₄₀ and Bi₂O₃, which are inevitable to overcome. As these secondary phases would affect its electrical properties, hence other techniques are considered, such as:

Liquid Phase Sintering [8]: Initial steps here are like a solid state route where pellets are sintering at about 880°C at a ramp rate of 100°C/s and held for 450s. Here it is Bi₂O₃ that accelerates the reaction being in liquid form as its melting point is about 817°C, and this high-rate kinetics allows for suppressing the formation of intermediate phases. This even suppresses the formation of oxygen vacancies, which avoid the formation of (Fe³⁺/Fe²⁺) couples which produce highly insulating samples.

Mechanical Activation [9]: Using planetary ball milling on precursor oxides for about 100 hrs leads to atomic scale mixing of the precursors and

forms a homogeneous amorphous mixture which leads to a reduction of sintering temperature to even about 700°C.

Spark Plasma Sintering [10]: Here, ceramics are densified at low temperatures, and that too only for a few minutes, which overcomes the possibility of decomposing BiFeO₃ into $Bi_2Fe_4O_9$. Also, it reduces Bi volatilization and the reduction of Fe³⁺; this provides highly dense ceramics.

1.3 Introduction to BaTiO₃

1.3.1 History and Applications

Many electronic devices these days rely on the conversion of mechanical energy to electrical energy, such as in energy harvester applications, as seen in ink-jet printers, ultrasonic imaging transducers, medicinal therapies, and vibration control sensors. Although PZT found many uses in these applications as hazards of this material were realized, such as chronic poisoning even in small traces, it became urgent for ferro electricians to search for materials that are low cost and can be recycled. Further, as the European Union banned the use of lead by legislating policies like waste from electrical and electronic equipment (WEEE) and end-of-life vehicles (ELV). So now the aim was to reach a piezoelectric charge coefficient of about 250-550 pC/N, a high dielectric constant of about (>1000), and low dielectric loss (tan δ <0.01) as well as Curie temperature of about 300°C using lead-free electroceramics and achieving these functional properties.

Barium Titanate (BaTiO₃) was discovered in the era of World War 2 in different parts of the world at different time periods. Around 1941 in the USA and about 1944 in Russia and Japan and over the years, studies conducted on it showed it a promising material for multilayer ceramic capacitors due to its high dielectric constant and low loss characteristics, which resulted because of the small size and high charge on Ti⁴⁺ ion, which when given an off center effect can store a lot of potential energy [11]. In the 1940s, von Hippel in the USA and Wuland Goldman in Russia discovered ferroelectricity in BaTiO₃, which allowed it to be used in piezoelectric devices such as sensors and actuators, particularly actuators made from BaTiO₃, giving large generative forces and better response time and could function on simple Electric field and these qualities make them better than electromagnetic actuators. It also showed a positive temperature coefficient of resistivity (PTCR) which can be used in transformers as temperature regulating triggers. All these applications of BaTiO₃ have revolutionized the microelectronics and communications industry.

1.3.2 Crystal Structure and Significance

BaTiO₃ is a perovskite material with Barium (Ba²⁺) being in twelve coordination, Titanium (Ti⁴⁺) in six coordination, and oxygen being in 6 coordination as well, where it is surrounded by two titanium ions and four in-plane barium ions.



Fig 1.3.: (a) Unit cell of cubic (paraelectric) phase BaTiO₃, (b) Tetragonal (Ferroelectric)unit cell of BaTiO₃ with Ti⁴⁺ ion offset upwards, (c) Tetragonal (Ferroelectric)unit cell of BaTiO₃ with Ti⁴⁺ ion offset downwards.

Here both variants shown have a 180° difference in orientation. The crystal structure in BaTiO₃ changes with temperature such that it shows

polymorphic phase transition as well one where ferroelectric to paraelectric phase transition occurs in this manner:

Rhombohedral (R3m) to Orthorhombic (Amm2) at -90° C then Orthorhombic to Tetragonal (P4mm) at -5° C then Tetragonal to Cubic (Pm-3m) at 130°C. Such diverse phases of BaTiO₃ make it possible to be used for various applications ranging from low to high temperatures [12].

1.3.3 Reaction Mechanism

There are many routes to prepare BaTiO₃, such as solid-state reaction, oxalate coprecipitation, hydrothermal, sol-gel, and mechanochemical methods. Nevertheless, out of all these methods, the solid-state reaction route is considered popular due to its ease of synthesis and high-volume production. However, this method has drawbacks such as chemical inhomogeneity, agglomeration, and especially secondary phase formation, which affect electrical properties significantly. As in this research, we have synthesized BaTiO₃ using a solid-state route; we would consider the mechanism through which our initial precursors interact and form the required phase. Though various researchers propose many mechanisms, a study conducted in 2014 considers the thermodynamics of each reaction based on enthalpy of formation calculated from Gibbs Free energy which realizes whether any reaction is even possible at a certain temperature. The intermediate phase that is of concern here is Ba₂TiO₄.



Fig 1.4: Steps from (A) to (D) exhibiting the formation mechanism of BaTiO₃[13].

Step (A). This step shows a ball milled mixture of BaCO₃ and TiO₂.

Step (B). This step takes place at about 600°C to 700°C, where BaCO₃ starts to dissociate, and it shows the formation of BaTiO₃ and the release of CO_2 as a byproduct of the reaction.

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2$$
.

Step (C). In this step, particle rearrangement is observed, and new surface contacts of the agglomerates are created as CO_2 is trying to escape through a network of microcracks generated due to in-build pressure of the gas. This allows for new reaction zones to be created where new BaTiO₃ is formed, and an intermediate phase is also formed during this step in the zones where BaCO₃ is in excess.

$$2BaCO_3 + TiO_2 \rightarrow Ba_2TiO_4 + 2CO_2$$

If the XRD pattern of the powdered sample shows peaks of this intermediate phase, it shows heterogeneities in the powder.

Step (D). It is the step that occurs when long calcination periods are provided where the intermediate phase mentioned above reacts with remaining TiO_2 and converts to BaTiO₃ again.

$$Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3$$
.

This teaches us that to create $BaTiO_3$ with the least amount of intermediate phases, the particle size of $BaCO_3$ and TiO_2 should be controlled along with the calcination time.

1.3.4 Literature Review

(i). Based On Various Synthesis Techniques

a). Modified Combustion Process [14]: In this method, single-phase nanoparticles of BaTiO₃ could be obtained at a temperature of about 250° C, here due to self-propagating combustion of Ba²⁺and Ti⁴⁺ions in the presence of citric acid along with oxidant fuel system such as with ammonium nitrate solution a white powder is obtained on continuous heating of precursors of Ba and Ti. The nanocrystallites found here are in the range of 20-40 nm in size. The dielectric constant of this material is about 1280 at 1kHz, and the loss factor is near 0.01.

b) Hydrothermal Synthesis Using Different Barium Salts [15]: Here, using different salts of barium such as halides, acetate, nitrate and hydroxide salts, BaTiO₃ is prepared, and it was found that halide salts (I⁻, Br ⁻, Cl⁻) gave highest tetragonal content which resulted in room temperature dielectric constant value of 2960 at 1kHz. The synthesis temperature chosen here is 240°C, and particle sizes obtained here are 1-5 μ m. While the BaTiO₃ formed using chlorine-based salts have a high dielectric constant, the nitrate-based salt has the lowest loss factor.

c) Sol-Gel Process [16]: Using this process, morphology can be controlled of $BaTiO_3$ and good uniformity could be obtained even at low sintering temperatures due to higher chemical activity. Here barium acetate and tetra

butyl titanate are used as precursors. This overcomes the constraint imposed by the solid state route, where particle size becomes an issue due to high sintering temperatures, which causes agglomeration. It is also observed that grain growth occurs at comparatively lower sintering temperatures in the sol-gel method than that of the solid-state route due to high surface area, which allows for easier grain boundary diffusion. Here average grain size of 20 μ m is noted at 1300°C and this sample had a dielectric loss of 0.021 with a dielectric constant of 5500.

d) Two Step Sintering [17]: The density of ceramic is of huge concern while evaluating their electrical properties, and sintering techniques like spark plasma sintering and microwave sintering can be used to process fine grained ceramics but still assemble lots of defects and pores which affect the poling process. Hence here, a two-step process of sintering is chosen to attain a small grain size. Moreover, it was found that d_{33} is improved with decreasing grain size. This technique is used to produce smaller domain width with small areas of the domain wall, which allows better mobility response of these domains under an electric field, and a grain size of 1μ m is optimum because for values lower than that the volume of grain boundary increases resulting in a decrease in domain density and poor piezoelectric properties. The d_{33} value reported here is 519 pC/N for samples prepared with this sintering method.

e) Solid State Reaction [18]: Although the processing techniques mentioned above could produce fine grained ceramics of BaTiO₃ in the nano-range, this would have a domain width also low as well which allows easy domain wall motion, which gives a high piezoelectric coefficient. However, the density of such ceramics has also become an issue; largescale production and stoichiometry can be maintained using a solid-state route. In this work, researchers used ordinary BaCO₃ and TiO₂ to prepare fine-grained BaTiO₃ in the range of 2 to 9.5 μ m using sintering temperatures from 1180°C to 1300°C. Moreover, it was found that the dielectric constant was superior for the sample sintered at 1220°C of about 3400 at 1kHz, and loss factor was also about 1.6%, and the piezoelectric coefficient of about 419 pC/N, which is way superior from the reported one of 190 pC/N for conventionally prepared samples.

(ii) Based on Doping Strategies

Inclusion of isovalent atoms in BaTiO₃ helps produce samples with low loss characteristics, such as the substitution of Ca^{2+} in place of Ba^{2+} and Sn^{4+} and Zr^{4+} in place of Ti⁴⁺. It is done to achieve phase coexistence which can be used to enhance piezoelectric properties. It was found that substituting Ca2+ at the A-site results in an increase in Tc and suppresses the temperature at which orthorhombic to tetragonal transition occurs. The addition of Sn^{4+} showed a decrease in grain size as its high ionic radii, which reduces growth rates and its P-E loops showed sharp saturated behavior leaving no polarization imprint, which is good for piezoelectricity. Also, its E_c reduces, which makes it easier to pole, and this is due to a decrease in the c/a ratio, which allows for easier rotation of the domain [19].

When Zr^{4+} is added to BaTiO₃, a single-phase perovskite is obtained; also, the Curie temperature is higher than when Sn⁴⁺ is doped. Here, the ceramic becomes softer in terms of its domain rotating ability.

1.4 (1-x)BiFeO₃-x BaTiO₃ Solid Solution

After considering the requirements for a high-temperature piezoceramic that could give better functional properties, BiFeO₃ promised to be a better candidate due to its existence of both magnetic and ferroelectric orderings. However, as it shows the capacity to be semiconducting at room temperature, which interferes with the process of electrical poling, also leads to dielectric loss. This can be overcome by doping other ABO₃ perovskites to it. One important candidate for this is BaTiO₃, as it shows high dielectric constant and good ferroelectric properties as well. Another

essential feature of this solid solution is the occurrence of a morphotropic phase boundary region which shows the existence of two phases together at certain compositions [20].



Fig.1.5: Structural phase diagram of BFBT solid solution with change in BTO composition.

The structure is rhombohedral up to 67 mol% of BiFeO₃ and tetragonal for 6 mol% BiFeO₃ in this solid solution. The presence of these two phases provides better polarization properties, such as hard polarization reorientation in the tetragonal phase and larger lattice distortion in the rhombohedral phase due to octahedral tilting. In BFBT solid solutions, two different cations can occupy both A and B sites: here, Ba²⁺ in the A-site acts as a blocking cation for the movement of smaller Bi³⁺ cations consisting of lone pair electrons simultaneously competing from B-site cations such as Fe and Ti. Moreover, this struggle led to the formation of pseudo-cubic structures in BFBT solid solutions.



Fig.1.6: A schematic of BFBT solid solution crystal structure with two different polarization directions [21].

However, one issue persists while sintering these samples: Bismuth volatilization and Fe covalence, which creates oxygen vacancies in the sample and pathways for their motion. Moreover, this motion of oxygen vacancies creates pinning centers, which reduces domain wall mobility [22]. This would be observed in acceptor-doped perovskites and it affects the functional properties of these materials. This particularly increases dielectric loss, which researchers have tried to tackle using doping strategies. One most common agents is manganese doping of about 1 mol% MnO₂, as this suppresses the formation of Fe²⁺_{Fe}³⁺and V^{**}o², which gives better polarizable properties to ceramics [23].

Strontium doping was conducted by Ge Wang et al., where it was found to increase W_{rec} and in a core-shell microstructure, but this also cultivated dielectric anomalies due to microchemical segregation [24]. Then the addition of rare earth at A-site or B-site substitution is done to overcome secondary phase formation, B.S. Kar et al. used Gd³⁺(Gadolinium) ions in the Bi³⁺ site, and it showed a decrease in crystallite size as gadolinium content decreases and grain size becomes smaller with an increase in
doping content as gadolinium inhibits the grain growth [25]. Dielectric loss increases at higher temperatures in Gd-doped samples; this arises due to the thermally activated relaxation process and space charge polarization across interfaces which increases due to grain growth inhibition in Gd-doped samples. Activation energy calculated from conductivity data shows maximum E_a for Gd doped samples of about 0.4572 eV.

Another rare earth lanthanum (La³⁺) doped by Ilkan Calisir et al., either as isovalent doping in the place of Bi^{3+} or donor-type substitution in place of Ba^{2+} , showed that isovalent doping produces a chemically homogenous structure. However, the donor-type doping showed a chemically heterogeneous, core-shell grain structure [26]. Here, the shell regions contain some changes in ferroelectric ordering and form nano-polar relaxor regions. Moreover, this core-shell microstructure impacts the ferroelectric polarization switching.

Degradation behavior like thermal degradation and time-based degradation called aging of BFBT samples were also conducted by Jianguo Chen et al. The aging phenomenon in ferroelectrics is a gradual reversal of domains due to space charge formation, ionic defects movement and reorientation of defect dipoles after poling [27]. It was found that BFBT ceramics with only rhombohedral R3c phase showed better thermal degradation and aging-based performance in comparison to BFBT samples which had a pseudo cubic phase in it. Another method is to produce ternary solid solutions along with BFBT. Wang et al. showed high resistivity in Nb₂O₅ doped BFBT in order to $10^{14} \Omega$ cm; also, the obtained P-E loops were slimmer, as observed in relaxor ferroelectrics.

1.5 Research Objective

All these techniques to enhance the functional properties of BFBT solid solutions are justified. However, in the end, it boils down to the charge conduction and relaxation mechanism, which contributes to higher dielectric loss, low polarization, and poor ferroelectric switching. As the reason for the reduction in insulation is given to the covalence of Fe ions and oxygen vacancies produced due to bismuth volatilization, another overlooked factor is the defects associated with the BaTiO₃. As BTO also shows oxygen vacancies formed during its sintering and Ti ion covalence present in it, these factors are also essential to be studied. To understand the propagation of charged defects of BaTiO₃ in BFBT solid solution, BaTiO₃ with different calcination time cycles are produced and then used as a component to form a solid solution. Another bottleneck is the stoichiometry of bismuth in these samples, which is also to be understood how much extra bismuth addition is sufficient to these samples and the response on various functional properties is registered. This culminates in 5 samples BFBT33_03, BFBT33_04, BFBT33_12, BFBT33_14, and BFBT33_16. Structural and electrical characterizations are done on these samples to conclude the effects of BaTiO₃ and Bismuth stoichiometry.

CHAPTER 2

Experimental Section

2.1 X-Ray Diffraction.

It is a technique using X-rays to study the crystal structure of the material in consideration. The feature exploited here is the angstrom range of wavelength, which is also in the same size range as interplanar spacings (d) of crystalline material. When X-rays interact with the powder form of the material, it interacts with the electronic structure of atoms and molecules. Moreover, this interaction produces a diffraction pattern as the distance traveled by X-Rays differs from each other by the difference of integral of wavelengths ($n\lambda$). The relationship which considers all these parameters is called Bragg's law given as:

$$n\lambda = 2dsin\theta$$

There are mainly two set-ups through which this measurement is done. One being the lab source where Copper based radiation is used, and the measurement is done in reflection geometry. While the other being the synchrotron-based source of X-rays which have greater intensity than lab sources and can be tuned to specific wavelengths. This high intensity of X-Rays can be transmitted through the bulk and large samples as compared to surface diffraction in lab sources. The structural characterizations for this work are conducted at Beamline-11 at Raja Ramanna Centre of Advanced Technology in Angle dispersive XRD (ADXRD) mode. In this facility, electrons move at about the speed of light in a circular ring and are kept in the ring using bending magnets. As the electrons are accelerated along a bent trajectory, they lose some energy in the form of X-Rays in the range of GeV. To achieve this feat, electrons are first injected into a linear accelerator and subsequently into a booster ring to achieve speed close to

the speed of light. Then this beam is transferred to a storage ring under a vacuum to prevent energy loss. When X-Rays are required at a certain place, bending magnets are placed, which allows the loss of energy in synchrotron radiation form in the tangential direction of the beam. Then inside the beamline monochromators made of silicon single crystal, slits and mirrors are placed to adjust wavelength and collimation. And then, after this beam is used for measurement, a MAR345 detector is used to capture the beam passed through the powder sample, as this mode works in transmission geometry. The wavelength of the beam used is 0.54Å for measurements taken of BFBT33 samples.



Fig.2.1: Single crystal silicon (111) channel-cut monochromator.



Fig.2.2: MAR345 detector imaging plate for collection of diffraction data.

2.2 Dielectric Measurements

Dielectric measurements are done based on the principle of the parallel plate capacitor method using an E4980A Precision LCR meter in a set up where dielectric material is placed between two electrodes to form a capacitor, and an alternating current field is applied. Then the LCR meter measures capacitance and dissipation coefficient (dielectric loss) from which relative permittivity, phase angle, impedance, and electric modulus can be calculated.

As the phase transition of BFBT solid solution occurs at a temperature of around 750 K to 800 K, a new dielectric measurement set-up was required. This led to the development of a high-temperature magneto impedance measurement set-up as part of an M.Tech. research project at RRCAT, Indore.



Fig.2.3: Three distinct views of magneto impedance measurement set up.

The main parts of the system are an aluminum chamber for housing electrical connections with 16-pin connectors for thermocouples and 4 terminal power supply. This stands on the base support and is bolted around the periphery; above the aluminum chamber stands the middle chamber for inlet and outlet ports of vacuum generation and release. A stainless-steel rod runs inside these chambers over which an asbestos Cshaped stub is placed to provide thermal insulation between the copper rod above, which houses the thermocouple and electrical connections and the stage for placing the sample whose measurement is to be done. To assess the thermal stresses and temperature distribution along the assembly and outside where a casing would be used to cover is done in ANSYS. This analysis showed that a temperature gradient of 500 K is observed between the steel rod inside and the casing outside.





On the stage, a clamping system made of gold clamps is provided, which can pivot around, and a rectangular quartz plate is positioned to place the sample.



Fig. 2.5: Clamping section of the sample with gold stoppers.

This whole assembly can be traversed over the stage below with a rail. This rail helps to slide the set-up back and forth. Moreover, on the rear end of this rail, a magnetic coil is placed, which can induce the magnetic field of 1 Tesla and be used to conduct magnetic measurements.



Fig.2.6: The above image shows the complete set-up of the magneto impedance measurement system.

The way dielectrics store energy is due to the polarization of dipoles. When an electric field is applied across the dielectric material, it does not allow electric charges to pass through it. But instead, a charge asymmetry induces in the material called polarization, where positive charges shift towards the applied electric field, and negative charges shift away from the field, creating a charge dipole. The relation between polarization (P), dielectric displacement (D), and applied electric field (E) is given as:

$$P = (\varepsilon_r - 1)\varepsilon_o E$$

Here ε_0 is the permittivity of free space (8.854 x 10⁻¹² F/m), ε_r is relative permittivity which is the ratio between material permittivity ε (Farad/meter) to that of free space ε_0 . And it tells how efficiently a dielectric store charge between parallel electrodes compared to these parallel electrodes being separated by a vacuum. It is a dimensionless quantity and is often referred to as the Dielectric constant. When a dielectric is subjected to alternating voltage, it induces a complex quantity called relative permittivity, ε^* . The real part ε denotes energy storage, and the imaginary part ε denotes energy loss due to leakage or dielectric absorption. Dielectric loss can be calculated using these two quantities,

$$\tan \delta = \varepsilon \, ``/\varepsilon \, `$$

This quantity determines how lossy a material is, and as this value approaches zero, it becomes an ideal dielectric.

The formulas that are used to determine various parameters using only Capacitance (C) and Dissipation factor (D_f) are as follows

(i). For dielectric constant (or real part of relative permittivity)

$$\varepsilon = \varepsilon_r = (C^*d)/(\varepsilon_o^*A)$$

Here d is the thickness of the sample, and A is the area of the electrode.

(ii). Phase Angle (θ)

$$\theta = \cot^{-1}(D_f)$$

(iii). Imaginary part of relative permittivity

$$\varepsilon$$
 " = ε ' cot θ

(iv). Complex Electric Modulus (M*)

$$M^* = 1/\epsilon^* = M' + j M''$$

M'=
$$\varepsilon'/[(\varepsilon')^2 + (\varepsilon'')^2]$$
 and M'' = $\varepsilon''/[(\varepsilon')^2 + (\varepsilon'')^2]$

This quantity is associated with dielectric relaxation and is the opposite of polarization. It talks about the decay of the electric field inside the material, which causes changes in the dielectric displacement vector.

(v). Complex Impedance (Z^*)

The real and imaginary parts of complex impedances can be calculated using the relation between Modulus and impedance. Here ω is the angular frequency, and C₀ is the capacitance when the sample geometry is considered, but the dielectric is the vacuum.

$$M' = \omega * C_0 * Z''$$
 and $M'' = \omega * C_0 * Z'$

Polarization Mechanisms of Dielectrics: Four mechanisms govern polarization in dielectrics and are listed below in order of increasing response time.

(i) Electronic Polarization: When alternating electric fields with frequencies in the ranges of 10^{15} to 10^{17} Hz are applied, the electron cloud in an atom gets displaced; this microscopic mechanism of polarization has a very fast response time.

(ii) Ionic Polarization: This occurs in ionic solids when cations and anions displace from their equilibrium positions in response to the electric field with frequency in the range of 10^{12} to 10^{14} Hz.

(iii) Dipolar Polarization: As in polar dielectric materials, negative and positive charge centers do not coincide but instead have a permanent dipole oriented further in the presence of the electric field. Due to thermal agitation causing this dipole, it becomes a temperature-dependent process. Relaxation phenomenon is observed in polar dielectrics at about 10^7 to 10^{10} Hz frequencies.

(iv) Space Charge Polarization: When charge carriers are trapped at grain boundaries in ceramics or interfaces, and an electric field is applied in the frequency range of 10^6 to 10^9 Hz, these trapped charge carriers cause charge separation across grains. This polarization mechanism can be associated with a high dielectric constant in the material.

2.3 Ferroelectric Measurements

Ferroelectric materials are a special class of polar dielectrics that only have one unique polar axis and are observed in 10 out of 32 defined point groups of symmetries. In the absence of an electric field, the spontaneous polarization vector of charged dipoles could be observed in the minimum of two equilibrium orientations in ferroelectrics. These materials offer reorientation and reversal of spontaneous polarization vectors in the presence of an electric field.

Phase transitions are observed in ferroelectric materials as they transit from the high-temperature paraelectric phase with higher symmetry to the lowtemperature ferroelectric phase with low symmetry, and this transition point is called the Curie point. The relationship which associates dielectric permittivity with temperature is given by Curie-Weiss law:

$$\varepsilon = \varepsilon_0 + (C/T - T_0) \approx (C/T - T_0)$$

Here C is the Curie constant, and T_0 is the Curie-Weiss temperature; it is evident from the above expression that as $T_0 \ge T_c$, the dielectric permittivity decreases. This phase change creates regions inside a crystallite to minimize electrostatic and elastic energies, which exhibit polarization of electric dipoles in the same direction called domains. When two domains with different polarization vectors meet, the interface is called domain walls. The directions of distinct spontaneous polarization are a function of point group symmetry, but the two common ones are 180° walls with oppositely oriented polarization and 90° walls with orthogonally oriented polarization.

Hysteresis Loop: It is the fingerprint of every ferroelectric material. As in ferroelectric material, reorientation of the polarization vector can be achieved under the presence of the electric field.



Fig. 2.7: Polarization – Electric Field Hysteresis Loop of ferroelectric material where a) to e) represent different polarization configurations.

There are certain parameters worth noting in the above loop, such as saturated polarization (P_s), remnant polarization (P_r) and coercive field (E_c). As the external field exceeds this value of E_c a polar state is gained in ferroelectric material, and increasing this field allows domain switching, which produces a significant change in the polarization and gets to the point of saturated polarization P_s attaining macroscopic polarization, at this point ceramic exhibit behavior like a linear dielectric. From this point, as the field gets to zero, the net polarization still doesn't attain a zero value, called remnant polarization. To attain zero polarization, a sufficient magnitude of field in opposite direction is to be applied, called coercive field (E_c). Based on types of conduction mechanisms, P-E hysteresis loops of type of materials are given:



Fig. 2.8: Current –Electric Field and Polarization-Electric Field hysteresis loops of (a)(b) linear dielectric, (c)(d) ferroelectric, (e)(f) Conductive material [28].

Here, linear dielectric shows a nearly rectangular box resulting from no permanent dipoles in I-V Loop; hence, the P-E loop shows a slim loop with no remnant polarization. Moreover, a typical ferroelectric increases its current value in the I-V curve resulting from domain switching near coercive fields. As the field further increases, the current drops to zero, indicating saturated switching of domains. Moreover, the third pair shows I-V and P-E loops of electrical conductivity. Furthermore, these three-conduction mechanisms contribute to whatever feature one observes in hysteresis loops.

(i)Normal Ferroelectric: It has large ferroelectric domains and strong dielectric nonlinearity. As the electric field is applied, alignment of the ferroelectric domain occurs. However, domains alone cannot return to their initial state due to the clamping of the domain wall. It produces high P_r and E_c as most of the energy cannot be released, so W_{rec} is low and is efficiency (η) .

(ii)Relaxor Ferroelectrics: It has different cations in similar crystallographic sites. Due to dielectric relaxation, the phase transition

occurs over a range of temperatures (T_m) instead of T_c curie temperature. It is observed that as frequency increases, the temperature T_m where ε_r occurs also increases. The presence of other cations in the A or B site in a perovskite gives disturbance in long-range order and produces Polar Nano Regions (PNRs), which have higher dynamics than the normal ferroelectric domain. This gives low P_r and low E_c , also high η with moderate P_{max} and $W_{rec.}$



Fig. 2.9: P-E Loops of different types of ferroelectrics are shown here [29].

(iii) Antiferroelectrics: These contain anti-parallel dipole alignment at two subsequent crystallographic lattice sites, resulting in zero polarization in the innate state or before applying an electric field. However, as an external electric field is applied transition from the antiferroelectric phase to the ferroelectric phase is observed, and this causes microscopic polarization. As the electric field is again reduced below a certain critical value, a reverse transition from ferroelectric to antiferroelectric phase is observed, and these transitions result in double P-E loops with near zero P_r and high P_{max} , which results in low η .

(iv) Relaxor Antiferroelectrics: It is observed in relaxor ferroelectrics that they have high η and a moderate W_{rec} and also observed in antiferroelectric

that they possess high W_{rec} but low η . Also, this creates relaxing characteristics and induces nano domains. Once again, a transition like a relaxor antiferroelectric to antiferroelectric and vice versa occurs, giving high P_{max} . This produces narrow P-E loops with linear polarization under low electric fields, giving high W_{rec} and η under high electric fields.

Here the measurement of P-E hysteresis loops is done using a radiant ferroelectric tester. Where samples of the BFBT33 series were cold pressed into pellets, and a wafer of 400μ m was used with silver paste coated on it with an area of 0.19625 mm² and kept in a silicon oil bath in between electrodes which were preheated at 150°C to remove moisture and to provide an insulating environment. The electric field applied is for 100Hz, and voltage ranges from 500V to 2000V.

2.4 Synthesis Process

A solid-state reaction route was chosen to synthesize the solid solution of BFBT33. There are two routes mentioned in the given flowchart; out of the two, it is one where $BaTiO_3$ is mixed with the precursor of Bismuth, and Iron oxide is used.



Fig. 2.10: Schematic of the synthesis process of BFBT33 solid solution.

The furnace used in this synthesis process is a box furnace, and the crucibles used were alumina. Zirconium oxide containers are used with zirconium oxide balls to do ball milling. The balls are added in the ratio of 5:1 (balls: powder) in the powder and isopropyl alcohol. Here, initial ball milling aims to achieve mechanochemical activation and homogenous mixing so that reaction kinetics could be better. The precursors taken are Bi_2O_3 (99% pure), Fe_2O_3 and for $BaTiO_3$ it is $BaCO_3$ and TiO_2 . Here BaTiO₃ is prepared in the same way as BFBT33 using solid-state reaction, and the calcination temperature is 1150°C for 12 and 6-hour calcination cycles, which also have ball milling in between and this sample is known as BTO (01) MT while another sample of BaTiO₃ is calcined for 6 and 4 hours and this sample is known as BTO (01) _LT with subsequent ball milling in between every calcination stage. Also, the stoichiometry of Bi₂O₃ is increased by 1% and 2% compared to Fe₂O₃ in samples of BFBT33. This leads to the creation of 5 samples of BFBT33 which are used for further characterization.

2.5 Field Emission Scanning Electron Microscopy (FESEM)

This morphological imaging technique uses an electron beam to scan the surface of the sample and show features on the surface, such as grain and grain boundaries on ceramics and nano-level morphology on samples synthesized with other methods, such as hydrothermal synthesis. As the electron beam interacts with the surface of the sample, this produces X-Rays, backscattered electrons and secondary electrons. Moreover, each one of these resultant products gives distinct information. Secondary electrons are used to have information about the topography of the material surface, resulting from inelastic collisions. While backscattered electrons are generated due to elastic collisions and a scattering of primary electrons, these can be used to unravel composition differences in the sample. The electron beam generated in FESEM uses a strong electric field; it contains high potential and is made to focus on the sample using a magnetic lens

and deflection coils. A detector receives the electrons produced after the interactions with the sample and converts them into electric signals that can be interfaced with a computer and observed. 10 nm gold coating on the pellet sample of BFBT33 is done to overcome the charge concentration effect and observe the features of ceramics. The FESEM used here is JEOL JSM-6500F.

2.6 Electrochemical Characterization

These characterizations can understand the behavior of the material when turned into an electrode to be used where electrochemical reactions cause charge storage. Unlike a dielectric used in solid-state ceramic capacitors, an electrolyte is used here. Potential, charge and current are the specifics that help explain the behavior of the material. Application of electric potential across the electrode and analyzing the current passing through it is the way to characterize any electrode. There are two types of setups to do this, two and three-electrode configurations. Two electrode configurations have one working electrode and the other counter electrode. If we want to study the working electrode, we polarize it either cathodically or anodically by applying current or voltage. We need a reference electrode whose potential can be kept constant to do this. Now, after applying a potential to the working electrode, we would want to learn about the current developed across the working and counter electrode, which completes the circuit. If the counter electrode is also participating in the flow of the current through it, then it will no longer be at constant voltage and hence no longer be able to apply voltage to the working electrode. So, we need an electrode that does not allow current to flow through it but also needs an electrode that can complete the circuit but whose analysis is not under consideration. Another electrode, called a counter electrode, is proposed, which is used to complete the circuit and carry the current. This gives an idea of three electrode systems and the information on reactions occurring at certain potentials. As the reference electrode is at constant potential and negligible current is passed through, the internal resistance (iR) drop between the reference and working electrode is relatively low, providing stable potential at the working electrode. Ag/AgCl and standard calomel electrodes are reference electrodes commonly used. Listed below are electrochemical techniques to analyze energy storage behavior.

2.6.1 Cyclic Voltammetry (CV)

In this technique current induced in the working electrode is recorded regarding the potential applied to it. Potential at the working electrode is increased gradually till a point where water dissociation in the electrolyte is observed. This would be the point where overpotential is reached, and hydrogen or oxygen evolution is seen. The potential is also decreased linearly to its initial position, and current is recorded while applying potential. Different rates at which potential is applied can be used to observe the kinetics of charge storage. Each charge storage mechanism, whether an electric double layer (EDLC) capacitor, pseudo capacitor or a battery type of faradaic charge storage mechanism, has a distinct feature in the CV curve.

EDLC shows a rectangular CV curve, while pseudocapacitive material shows broad oxidation-reduction spikes at around the same potential. In battery-type materials, peaks of oxidation and reduction are observed at different potentials. The area enclosed by the CV curves gives specific capacitance and the expression for calculating it:

$$C_s = 1/(m^*\Delta V^* v) \int_{V_1}^{V_2} i dV$$

Here the integral gives the area under the CV curve, m being the mass of the electrode in grams (g), $\Delta V = V_{1-}V_2$ potential window (Volts), and v is the scan rate (V/s)



Fig. 2.11: Cyclic Voltammetry and Galvanostatic charge-discharge curves of EDLC, pseudocapacitive and battery type of material [30].

The current response of the working electrode at any scan rate consists of two processes, the first being the slow diffusion-controlled process ($i_{diff.}$), where a certain number of particles diffuse through an area. It is proportional to the concentration gradient across the area, while the other process is adsorption, where electroactive species migrate from the bulk to the interface, such as double-layer charging at the electrode surface or redox reactions on the surface (i_{cap}). It can be written as:

$$i = i_{\text{diff.}} + i_{\text{cap}} = a v^{b}$$

 $\log i = \log a + b \log v$



Fig. 2.12: Log (i_p) vs. Log (v_s) plot for determining major charge storage mechanism.

Here a and b are constants; when the b value is near 1, it means that charge storage is mainly due to surface faradaic reactions and double-layer behavior, whereas if b is close to 0.5, then the diffusion-controlled process governs energy storage as observed in batteries.

2.6.2 Galvanostatic charge Discharge (GCD)

Like cyclic voltammetry, this technique can be used to evaluate specific capacitance and the nature of reactions occurring at the surface of the electrode. On application of constant current, the electrode is charged and discharged continuously, and change in its potential is measured with respect to time. If the variation of potential with time is linear and a triangular shape is observed, then it shows the presence of fast surface redox reactions like EDLC. If a plateau is observed, diffusion-controlled behavior is in command. Using the area under the curve of the GCD curve, one can calculate specific capacitance using the following relation:

$$C_{\rm s}=1/m\int_{V1}^{V2} \frac{1}{v}dt$$

2.6.3 Electrochemical Impedance Spectroscopy (EIS)

This technique can be used to characterize electrode impedance behavior. An AC signal of a small amplitude of about 0.5V is applied in the frequency range of 10mHz to 100,000 Hz, and associated impedance is captured. Using EIS, two general plots are developed: the Bode plot, which is between phase angle and frequency, and the Nyquist plot, which is between real and imaginary impedance. Nyquist plot exhibits three distinct features for electrochemical systems: a semi-circular curve in the high-frequency region which gives equivalent series resistance where the semicircle start intersects on the real axis and its diameter give charge transfer resistance, a line with a 45° slope in the mid-frequency region which is Warburg Impedance and another line in the low-frequency region with a slope near to 90° , which indicates capacitive EDLC behavior. The electrochemical measurements done for this work are in a threeelectrode configuration. The electrode was prepared using powder of BFBT33 samples of about 10 mg and sonicating it with 200μ L of ethanol and 20μ L of Nafion binder. Then this composition was drop cast on Nickel foam (1cm x 1cm) with about 2mg of mass loading, and the electrolyte chosen is 2M KOH to conduct electrochemical studies on workstation Autolab, PGSTAT204, Metrohm. Here platinum wire worked as a counter electrode, and a Standard calomel electrode was used as the reference electrode.

2.7 Piezoelectric Measurements

Piezoelectricity is the ability of crystalline substances that develops an electrical displacement, D, which is proportional to applied mechanical stress, σ . This effect is known as the direct piezoelectric effect when a mechanical strain (S) is induced by applying an electric field (E).



Fig. 2.13: (a) Direct Piezoelectric Effect (b) converse piezoelectric effect © direction indices of constants in poled ceramics.

The relationship between vector (D or E) and tensor (σ or S) is completed using coupling coefficients d_{ijk}, which is a third-rank tensor. Here (*i*, j k= 1,2,3):

$$D_{i} = d_{ijk} \sigma_{jk}$$
$$S_{ij} = d_{kij} E_{k}$$

Here D_i is electric displacement along *i* -axis due to the application of stress σ_{jk} and d_{kij} is piezoelectric charge coefficient. As piezoceramics exhibit maximum coupling along a specific direction, the properties can be described using two subscripts, one for electrical and mechanical parameters. The most common one is d_{33} , where electrodes are kept perpendicular to axis 3, and the applied field is also along direction 3.

To get better electromechanical coupling, poling of ceramics is to be done where domain alignment occurs under the presence of the electric field. This process is called poling. A new polarization is achieved in the direction of the electric field. Poling for BFBT33 ceramics is done using a setup submerged in silicon oil to create an insulating environment, and a field is applied in the range of 0.6KV on a 400 μ m sample with silver paste coated on it. Measurement of d₃₃ is done using a tester which applies a load of about 1N and response of the sample is measured.

CHAPTER 3

RESULTS and DISCUSSION

3.1 X-Ray Diffraction



Fig. 3.1: Synchrotron-based XRD Plot of BFBT33 Samples carried out at λ = 0.49Å (a) XRD Plot of all samples, (b) Zoomed plot between [110] and [111] peak, (c) Le Bail fitting of P m -3 m and R3c phases together, (d) Le Bail fitting of P m -3 m phase (e) Le Bail fitting of R3c phase.

The XRD results show that no secondary phases are formed in any of the samples, such as Bi₂Fe₄O₉ andBi₂₅FeO₃₉, which are Fe and Bi rich. Presence of these secondary phases affect electrical properties. Le Bail fitting was done to determine whether two phases coexist or not [31]. First, using single phases such as P m - 3 m, R3c and then considering both. The fitting results showed that good fitting was observed when both phases were considered and not when fitted for each phase single-handedly. This fitting helped to give the lattice parameters of both the phases present in the solid solution. The lattice parameters obtained through the result of the fitting show no significant change in their values and the c/a ratio of the rhombohedral phase does not show significant change; hence, the addition of bismuth does not significantly affect the unit cell size. Also, the calcination time of BaTiO₃ used as a precursor to prepare the solid solution does not show any change in the lattice parameters. Hence structural characterization of these five solid solutions are indifferent from each other. Below given table provides the information about the unit cell parameters of both the phases coexisting in the samples.

Sample	Pseudo Cubic (P m –3 m)			Rhombohedral (R3c)		
	a	b	c	a	b	c
BFBT33_03	3.994	3.994	3.994	5.6381	5.6381	13.8633
BFBT33_04	3.9912	3.9912	3.9912	5.6425	5.6425	13.8461
BFBT33_12	3.9941	3.9941	3.9941	5.6504	5.6504	13.8419
BFBT33_14	3.9909	3.9909	3.9909	5.6518	5.6518	13.8121
BFBT33_16	3.9921	3.9921	3.9921	5.6687	5.6687	13.8245

Table 3.1: Unit cell parameters of BFBT33 samples.

3.2 FESEM Results



Fig. 3.2: Scanning Electron Micrographs of all BFBT33 samples:(a) BFBT33_03, (b) BFBT33_04, (c) BFBT33_12, (d) BFBT33_14, (e) BFBT33_16.

The above images show bimodal grain distribution in all five samples of BFBT33 [32]. It is observed from the above samples that with the increase in bismuth content, the grain size increases. The lower melting point of Bi_2O_3 of about 817°C is the reason for increased grain size due to extra bismuth addition, which forms a liquid phase near grain boundaries and lowers the sintering temperature promoting densification of grains. And the effect of using $BaTiO_3$ with different calcination period have no significant effect on the grain size of these samples.

3.3 Dielectric Measurements



8000 -4000 -0 - - -400

3.3.1 Dielectric Constant and Dielectric Loss

Fig. 3.3: BFBT33 samples Dielectric Plots at five different frequencies.

600

т (in K) **BFBT33** 16

700

800

500

The above plots show that only the BFBT33_04 sample shows transition at a mean temperature of about 750K for the five frequencies shown here. This is the sample with the highest dielectric constant among all five samples. Addition of 1% extra bismuth helps reduce the loss and as this quantity increased to 2%, the decrease in dielectric constant was observed. While the sample which consist of BTO (01)_MT, showed comparatively lower dielectric constant and higher loss characteristics than other samples. The reduction in dielectric constant and increase in loss could be due to higher calcination time for samples having BTO _ (01) MT, which was calcined for a longer calcination period which could induce more oxygen vacancies compared to the sample which was calcined for shorter periods. As oxygen vacancies increase, the hopping mechanism becomes dominant for charge carriers movement, which increases dielectric loss and as dielectric loss increases, the polarization of dipoles becomes difficult, reducing dielectric constant [33].



Fig. 3.4: Dielectric loss plots of BFBT33 samples.

Dielectric loss plots indicate that after increasing Bismuth content from stoichiometry to 1%, a drastic decrease in dielectric loss is observed, but as 2% extra was added, so loss increased again. Also, the sample with BTO (01) _ MT instead of BTO (01) _ LT has more loss. BTO (01) _ MT samples show the same effect of bismuth addition. This loss pattern can be attributed to excess bismuth, which could have Bi₂O₃ left in it as a secondary phase which reduces the dielectric constant and increases dielectric loss as well [36]. To compare these 5 samples with each other, we have a comparison plot, these two plots show that sample BFBT33_04 consists of better dielectric constant and loss properties compared to other samples.



Fig. 3.5: Dielectric Constant and Dielectric Loss plots.

3.3.2 Impedance and Modulus Spectroscopy

These techniques are used to learn about impedance behavior, which tells us how much any circuit would resist the flow of electrons. Here we would consider the imaginary part of impedance, which gives us the value of reactance change with frequency. Then modulus spectroscopy gives us information about dielectric relaxation. By calculating activation energy from these plots, we gather an understanding of mechanisms that govern the loss and relaxation mechanisms in the ceramic. Below the imaginary part of impedance plots with respect to frequency can be seen at a certain temperature range



Fig. 3.6: Impedance Spectroscopy plots for all BFBT33 Samples.

The above plots show that as temperature increases, the plots shift towards a high-frequency region at its transition point where resonance occurs, showing a typical capacitor-type behavior. As temperature increases, impedance also decreases, showing thermally dependent impedance behavior. Here also, we can see the BFBT33_04 sample shows the highest resistance for the recorded temperature of 530K at 10kHz in the range of 4000 ohms. Modulus spectroscopy plots are shown below to assess the dielectric relaxation.



Fig. 3.7: Modulus plots of all BFBT33 samples.

The above plots convey that as temperature increases, the frequency at which transition from long range order to short range order motion of the charge carrier also increases, and the modulus value drops. On increasing Bismuth content to 1%, a drastic decrease in the frequency at which transition occurs is observed from 4985Hz to 431Hz for the data at 450K. This tells that the addition of bismuth reduces the frequency, which increases relaxation time, the time required to reach equilibrium orientation. As this relaxation time increases, it increases dielectric absorption, meaning it takes more time for dipoles to polarize over the

changing electric field. This holds off the electric field and does not allow it to decay quickly. Activation Energy Plots of impedance and modulus are shown below:



Fig. 3.8: Activation energy plots acquired from impedance and modulus plots with frequency.

From the above plots, it is evident that the value of activation energy lingers between 0.45 eV to 0.6 eV and this is usually assigned to oxygen vacancies in ABO₃ perovskites [34]. The activation energy increased after adding 2% bismuth to BFBT33 samples with BTO (01) _ LT. However, the samples with BTO (01) _ MT showed reduced activation energy. After considering dielectric loss, modulus plots and activation energies, we can conclude that adding 1% Bismuth to samples with BTO (01) _ LT is beneficial for its properties. Formalism of Z'' with M'' is plotted to gain insight in the activation energy difference obtained from impedance and

modulus spectroscopy, here the difference in its peak frequency values gives insight into whether the charged carriers motion is localized or delocalized.



Fig. 3.9: Z" vs. M" formalisms for all BFBT33 samples.

The differences in the peak frequencies for the Z'' and M'' values in the above plots give information about the charge conduction and dielectric relaxation mechanism. If the difference is high, the difference in value of activation energies calculated from impedance and modulus spectroscopy would also be high. This converges with the fact that the charge carrier movement is localized in the sample and is not of long-range order. This is observed in the BFBT33_04 sample, which showed the highest value in the difference of 0.7, while the lowest values are shown by samples that

have BTO (01) _ MT in them of about 0.6; this means that the activation energy difference would also be low for these samples and they exhibit delocalized charge carrier movement. Hence making a BFBT sample with BTO (01) _ LT and adding only 1% extra bismuth in it is an excellent choice to induce localized charge species movement where it is useful.

3.4 Ferroelectric Measurements



Fig. 3.10: P-E hysteresis loops of BFBT33 samples and comparison of all samples at 45k V/cm.

In the P-E hysteresis loops shown above, only BFBT33_04 shows a typical ferroelectric response, and all other samples show features of electrically conductive loops at higher electric field values. The feature observed in these samples where the polarization reduces at higher fields occurs as at high fields, dipoles cannot hold the charges and relaxes, due to which a dip in the value occurs. Samples with BTO (01) _ MT in it show lossy behavior. Only the BFBT33_04 sample can be used for high-power transducers and high-field actuators [37] as it has a high coercive field.

3.5 Electrochemical Measurements

The samples of BFBT33 were electrochemically analyzed using three electrode systems: calomel electrode as the reference electrode and platinum wire as the counter electrode. The working electrode was prepared using a drop cast of the slurry of BFBT33 samples in Ni form. Using 2 M KOH alkaline aqueous electrolyte ranging from 0 to 0.45V with electrode mass loading of about 2 mg/cm².

3.5.1 Cyclic Voltammetry

The CV curves of BFBT33 samples recorded at different scan rates from 5-100 mV/s in the potential range of 0-0.45 V are shown in Figure 3.1. The reversible redox (oxidation and reduction) peaks signify faradaic reactions occurring between Fe^{2+}/Fe^{3+} and $Bi^{3+}/Bi^{0,}$ and the OH- in the KOH electrolyte may be involved and through either of this reaction [35]:

 $FeO + OH^- \leftrightarrow FeOOH + e^-$

$$Bi + 3OH^- \leftrightarrow BiOOH + H_2O + 3e^-$$



Fig. 3.11: Cyclic Voltammetry plots of all the samples, also a comparative plot of all the samples at 10mV/s scan rate.

As scan rates are changed, the symmetric and reversible shape of the CV curve suggests rapid charge transfer at the electrode and electrolyte interface during the faradaic reaction mechanism. With an increase in scan rates, the area of the curves continues to increase, as predicted by the Randles-Sevcik equations. Here reversible curves show that charge transport at the electrode-electrolyte interface comprises both polarization and surface redox reactions effect. The scan rate-dependent variation in the

specific capacitance of BFBT33 samples from their respective CV curves from the equation,

$$\mathbf{C}_{\mathbf{s}} = \frac{\int_0^{0.45} \mathbf{\Box} i \, dv}{m \, v \, \Delta V}$$

Where Cs represents the specific capacitance (F/g), m represents the mass of active electrode materials (g), v represents the scan rate (V/s), ΔV represents the potential range (V), and idv represents the integral area of the CV curve. Among all the samples, it is BFBT33_04 that showed the most symmetric CV curve and the highest specific capacitance of 173 F/g at 5mV/s of scan rate.

Current can be represented as the sum of the currents resulting from the quick surface redox reaction (K_1v) and the slow semi-infinite diffusion-controlled contribution process $(K_2v^{1/2})$ under the potential sweep rate. This is how an empirical relationship is provided:

$$i_p = av^b = K_1v + K_2v^{1/2}$$
.....(a)
or log $i_p(v) = \log a + b \log(v)$(b)


Fig. 3.12: a) Specific capacitance at various scan rates. b) log of peak current density (i_p) vs. log of scan rate.

Where a and b are constants, the scan rate is s, and the current density is i_p. If b is 1, then it represents the current-controlled capacitive process; if b is estimated to be 0.5, then it represents the semi-infinite diffusion-limited process; and if b is estimated to be 0.5 - 1, then it represents a transition region that combines capacitive and battery properties. Here the sample BFBT33_04 showed the highest specific capacitance of about 173 F/g at 5mV/s which exponentially reduces to 45 F/g at 100 mV/s; the reason for this reduction is that at higher scan rates, the OH⁻ ion would experience a barrier to reach deep into the surface, which restricts the redox reactions to occur at such faster scan rates. From the results it is evident that the higher the polarization, the better the absorption of OH⁻ ions on the surface. Here, oxygen vacancies are suppressed, but oxygen vacancies are active sites for

faradaic mechanisms to occur, increasing ionic conductivity. But too much bismuth is also not favorable as this allows reduction of bismuth on interaction with OH^- to occur Bi^{3+}/Bi^0 , which releases three electrons which then reduces polarization, and the value of b drops to 0.55 and the storage relies more on diffusion mechanism as seen in BFBT33_14 sample. Hence it is due to contribution of both the polarization and the surface redox reaction that stores the energy in BFBT33 solid solution samples.

The BFBT33_03 sample showed that it relies heavily on surface redox reaction mechanism, as it has lower polarization than BFBT33_04, but oxygen vacancies contribute to good ionic conduction. While the samples which have BTO (01) _ MT show lower capacitance as it already has higher oxygen vacancies content. Also, its high dielectric loss retards the polarization, which is overrun by faster surface redox reactions which further reduces polarization and reduces capacitance further. Hence BFBT33_16 sample shows b about 0.48, which is evident of its battery type character.

3.5.2 Galvanostatic Charge Discharge

In Fig 3.13, the current density dependent C_s values were evaluated from the GCD curves using the equation [38],

$$\mathbf{C}_{\mathbf{s}} = \frac{I \, dt}{m \, dv}$$

Where Cs represents specific capacitance (F/g), I represent applied current (A), m represents the mass of loading on the working electrode (g), and dt/dv represents the slope of the discharge curve in GCD. These plots are helpful to compare these five samples in terms of their discharge time. The sample with higher discharge time would be better among all samples.



Fig. 3.13: GCD plots of BFBT33 samples at different current densities.

GCD studies were conducted on BFBT33 samples to assess the effect of different current densities on these samples and monitor their discharge time. Here the plateaus occur at different voltages for charging and discharging, which exhibit battery-type behavior of samples. BFBT33_04 showed a maximum specific capacitance of about 183 F/g at 1 A/g. The decrease in specific capacitance with the increase in current density is because, at high current densities, the ions in the electrolyte cannot diffuse into the electrode quickly. This sample showed the highest discharge time,

about 40 seconds, while others lingered for about 10 seconds. Better discharge time is due to its high polarization and low loss characteristics, which hold the electric field and does not let it decay soon. Below shown are comparative GCD plots of BFBT33 samples here plots show the superior discharge time of the BFBT33_04 sample, and its high specific capacitance is evident.



Fig. 3.14: a) GCD curves of all BFBT33 samples, b) specific capacitance vs. current density samples.

Sample Sp. Capacitance (C _s), F/g	Scan Rate (mV/s)					Current Density (A/g)				
	5	15	25	50	100	1	2	3	4	5
BFBT33_03	55.4	43.4	36.6	28.5	22	87	33	22.2	14	13.2
BFBT33_04	173	144	128	105	44	183.4	158.5	144.8	132.8	114.2
BFBT33_12	53.3	41	33.7	23.7	16	58.2	40.3	21.5	17	10.6
BFBT33_14	51.1	37.8	30	20.1	14	53.7	32.5	20.6	19.4	17.17
BFBT33_16	52.3	37.2	28.4	18	11	53.70	26.82	20.7	12.3	7.56

Table 3.2: The value of Specific capacitance with scan rate and current density.

3.5.3 EIS and Ragone Plot

Along with the quantity of active elements and electrolytes, the electrical characteristics, core of the material, and textural boundaries are crucial to the effectiveness of energy storage. To comprehend the impact of materials and electrolyte resistance on ion diffusion on the BFBT, electrochemical impedance spectroscopic (EIS) research was carried out



Fig. 3.15: (a) Electrochemical Impedance spectra of BFBT33_04 sample on the electrode, (b) zoomed plot of EIS

EIS is conducted on the BFBT33_04 sample, which had the best supercapacitor performance among all electrodes, to understand reaction kinetics at the interface of electrode and electrolyte. The Nyquist plot above exhibits a semicircular region at high frequencies, with a line having a high slope at low frequencies. The circuit shown inside the EIS spectra

is used to fit the spectra where R_s is the resistance of bulk solution, R_{CT} is charge transfer resistance, Q is the constant phase element between electrode and electrolyte, W is the Warburg impedance, and C is faradaic supercapacitance. R_s is the intercept of the plot with the Z' axis giving resistance of solution and contact resistance between active material and current collector. The values of R_s and R_{CT} are 0.8701 Ω and 238.9 Ω , respectively. The charge transfer resistance is high in this sample due to high polarization, and the straight steep line shows that diffusion resistance is low.



Fig. 3.16: Ragone Plot of BFBT33_04 sample

The Ragone plot shows that the specific power density is about 8500 W/kg, and the specific energy density is about 5.2Wh/kg.

CHAPTER 4

CONCLUSION and FUTURE WORK

4.1 Conclusion

In this work, we synthesized two $BaTiO_3$ samples with different calcination times and used these two variants to produce five samples of 0.67 BiFeO₃-0.33 BaTiO₃ using solid state synthesis. The XRD pattern of these samples showed no signs of secondary phases, and the Le Bail fitting confirmed the presence of two phases that sit well in the region near the morphotropic phase boundary. The scanning electron micrograph of all the samples showed a bimodal grain structure with distinct grain boundaries and low porosity. The dielectric constant of the BFBT33_04 sample measured at 10kHz is about 32500 at 750 K with a dielectric loss (tan δ) of 0.34 at 500 K. Activation energy of this calculated using impedance spectroscopy sample comes to be about 0.44 eV which confirms the suppression of oxygen vacancy due to bismuth volatilization and 0.56 from modulus spectroscopy which entails that relaxation process is through some other mechanism. The ferroelectric hysteresis loop of BFBT33 04 sample measured at 10 Hz and 60 kV/cm exhibited a typical ferroelectric behavior with P_r = 32 μ C/cm², E_c = 30 kV/cm and P_{max} = 40 μ C/cm². To assess the electrochemical energy storage properties of the BFBT33_04 sample, the three-electrode configuration is used in 2M KOH electrolyte, which exhibited a combination of both capacitive and surface redox reactions along with battery kind of behavior, which is also evident from the CV curves showing reversible redox peaks. Galvanostatic chargedischarge showed the electrode specific capacitance C_s to be about 183 F/g at 1A/g current density. All these values convey that the defect chemistry that is part of BaTiO3 will be propagated in the BFBT solid solution.

Hence, before going to tackle the problem of Bismuth volatilization and Fe^{2+}/Fe^{3+} covalence, we should instead deal with issues observed at the BaTiO₃ level and understand mechanisms of charge conduction and dielectric relaxation to prepare a more insulating sample.

4.2 Future Scope

BiFeO₃-BaTiO₃ solid solution is a promising candidate for hightemperature piezoceramics for sensor and actuator applications. By understanding the effect of structure and defects on its polarization and leakage current dynamics, we can synthesize better samples. As we have established that reducing dielectric loss at the level of BaTiO3 would help avoid propagation of them in solid solution, we can equip strategies of substitution and better synthesis optimization to achieve better functional properties. Doping at A-site using Mg²⁺ and Ca^{2+ instead} of Bismuth and Na⁺ and K^+ instead of barium can avoid the Fe^{2+}/Fe^{3+} covalence. Also, doping at the B site using Zn^{2+} and Mn^{2+} for iron and La^{3+} in place of titanium could be done to avoid the hopping in the Ti^{3+}/Ti^{4+} pair. Another important thing to discover here is the mechanism of charge storage and use of ferroelectrics in electrochemistry and explore how it shows battery-type behavior instead of pure capacitive type and the redox reactions involved in it. Also, the effect of polarization on ion kinetics should be conducted. All these combined efforts will help create better lead-free electroceramics with novel functional properties.

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