

**SYNTHESIS AND CHARACTERIZATION OF BNT FERROELECTRIC  
CERAMIC BY AUTO-COMBUSTION TECHNIQUE**

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A Dissertation Submitted in partial fulfilment  
FOR THE DEGREE OF MASTER OF SCIENCE IN PHYSICS  
Under Academic Autonomy

**NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA**

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**May 2012**



**NATIONAL INSTITUTE OF TECHNOLOGY  
ROURKELA**

**CERTIFICATE**

This is to certify that the thesis entitled, “**Synthesis and Characterization of BNT Ferroelectric Ceramics**” submitted by Miss. Prajna Lipsa Moharana in partial fulfilments for the requirements for the award of Master of Science Degree in Physics Department at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the project has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

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Lastly my hearty thanks to my parents and my sister’s for their blessings, inspiration and moral support.

**Date:14.05.2012**

**Prajna Lipsa Moharana**

## **DECLARATION**

I hereby declare that the project entitled “Synthesis and Characterization of BNT ferroelectric ceramic by auto-combustion technique” submitted to the NIT, Rourkela, is a record of an original work done by me under the guidance of prof. S Panigrahi faculty member of NIT, Rourkela and this project work has not performed on the basis for the award of any other degree or diploma/associate ship/fellowship and similar project if any.

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M.Sc Physics

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## ABSTRACT

$(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$  was prepared by auto-combustion method, taking urea as a fuel with varying concentrations in different calcined temperature. XRD and SEM analysis was carried out to confirm the single phase and growth of the particles. At 25 wt. % of urea, pure phase of BNT was confirmed at  $700^\circ\text{C}$  but at 50wt. %, well intensified peak appeared with a little un-identified peak. Calcine temperature was reduced marginally in this fuel additive method. Powder prepared at  $700^\circ\text{C}$  was chosen for further study. Dielectric measurement of sintered pellet at  $1100^\circ\text{C}$  of durations 2hr, 3hr, 4hr were taken and analyzed as well as hysteresis measurement was carried out. Improved dielectric and ferroelectric property was seen of the pellet sintered at 3hr duration due to well grain growth.

## CHAPTER I

### 1.1 Motivation and Background

The large scale application of Ferroelectric materials in day to day life in capacitors, sensors, actuators, transducers and memory application demands novel materials of high dielectric constant with low dielectric loss, good piezoelectric as well as pyroelectric properties. Lead based compounds dominated the electro ceramic industries due to its exceptional peculiar properties. The high toxic nature of lead alarms the world for elimination of its use in various devices. The search for novel environmental friendly ferroelectric material is in demand. Bismuth Sodium Titanate(BNT),  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  was discovered with its good ferroelectric property, which may be considered as an alternative for lead based compounds.

Synthesis of BNT in solid as well as chemical route has been reported in several papers. Synthesis route plays a vital role in determination of particle size which will affect the various properties of interest. Preparation of BNT in auto-combustion method is a new way of controlling particle size which was studied intensively in this work.

### 1.2 Introduction

Ferroelectricity is a phenomenon of reversibility of spontaneous polarization which was discovered in 1921 in Rochelle salt. Therefore it shows a P-E hysteresis loop analogous to M-H loop of ferromagnetism, which is responsible for such naming. Ferroelectricity has also been called Seignette electricity, as Seignette is another name of Rochelle Salt (RS). Spontaneous polarization arises in non-centrosymmetric structural unit due to charge centre shifting on cooling below the Curie point. Ferroelectric materials like  $(\text{BaTiO}_3)$  are being used in piezoelectric transducer devices and capacitor applications. Many other ferroelectric ceramics including lead titanate  $(\text{PbTiO}_3)$ , lead zirconatetitanate (PZT), lead lanthanum zirconatetitanate (PLZT), and relaxor ferroelectrics like lead magnesium niobate (PMN) have also been developed and utilized for a variety of applications. With the development of thin film technology and

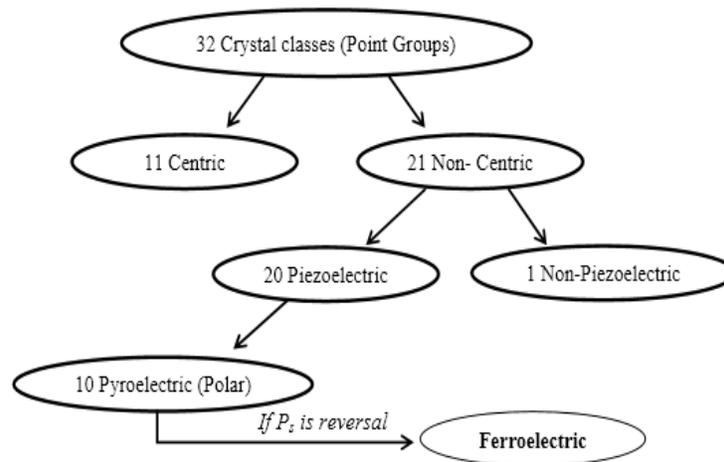
ceramic processing, many new applications have been developed. The most significant use of ferroelectric ceramics have been in the areas such as ferroelectric thin films used as non-volatile memories, ferroelectric ceramics used for capacitor applications, piezoelectric materials used for medical ultrasound imaging and fabrication of actuators, and electro-optic materials used for data storage and displays.

### 1.3. General properties of ferroelectric materials

#### 1.3.1. Crystal Symmetry

A crystal structure is the unique arrangement of atoms or molecules. Crystal symmetry consists of rotational symmetry, translational symmetry, and mirror symmetry. The lattice structure described by the Bravais unit cell of the crystal governs the crystal symmetry. There are thousands of microscopic symmetry types or space groups based on the symmetry elements [1, 2], out of which 230 have been grouped together. Most of the crystals possess symmetry elements in addition to the repetitions expressed by the crystal lattice.

Out of the 230 space groups that there is just 32 point groups. As shown in Fig 1, the seven crystal systems can be divided into these point groups according to the point group symmetry they possess.



**Fig. 1**

### 1.3.2 Spontaneous polarization and Pyroelectric effect

Ferroelectric materials show polarization even in the absence of electric field. This property is referred as spontaneous polarization. They show polar axis. In most of the non-centrosymmetric group (10 point groups), dipole moments are arranged in arbitrary manner results cancellation of each other's effect to zero. In the rest non-centro symmetric group, dipole moment of different orientation contributes in a particular direction called polar axis results existence of polarization in the absence of applied field. This is known as spontaneous polarization.

The materials possessing spontaneous polarization belongs to Pyroelectric group, which is basically thermal sensitive i.e. when there is a variation of temperature in the surrounding, the material gets polarized along its polar axis. Only crystals with a unique polar axis (10 out of 21 non-centrosymmetric point groups) show a spontaneous polarization vector  $\mathbf{P}_s$  along the polar axis. The value of the spontaneous polarization depends on the temperature. This effect is known as the pyroelectric effect, and was first discovered in tourmaline by Teophrast in 314 B.C. and so named by Brewster in 1824 [3]. The pyroelectric effect can be described in terms of the pyroelectric coefficient  $\Pi$ . A small change in the temperature  $\Delta T$  in a crystal in a gradual manner causes to a variation in the spontaneous polarization vector  $\Delta \mathbf{P}_s$  given by

$$\Delta \mathbf{P}_s = \Pi \Delta T \quad (3)$$

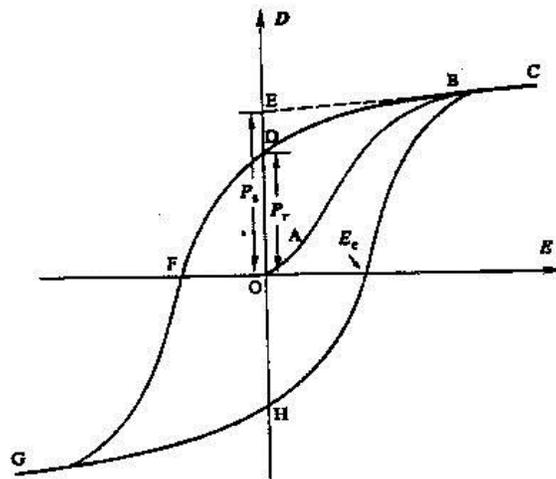
### 1.3.3 Ferroelectric domains & hysteresis loop

Pyroelectric crystals show a spontaneous polarization  $\mathbf{P}_s$  in a certain range of temperatures. The crystals whose magnitude and direction of  $\mathbf{P}_s$  could be reversed by an external electric field are said to show ferroelectric behavior. Therefore, all single crystals and successfully poled ceramics which show ferroelectric behavior are pyroelectric, but vice versa case isn't true. For example, tourmaline shows pyroelectricity but is not ferroelectric.

**Ferroelectric** crystals possess regions with uniform polarization called ferroelectric domains. All the electric dipoles within a domain are aligned in the same direction. Domains in a crystal are separated by interfaces called domain walls. When a ferroelectric single crystal is grown, it may have multiple ferroelectric domains. We can obtain a single domain by inducing domain

wall motion by the application of an appropriate electric field. Reversal of the polarization in the domain could occur due to a very strong field, known as domain switching. [4, 5]

**The main difference between pyroelectric and ferroelectric materials** is that the direction of the spontaneous polarization in ferroelectrics can be switched by an applied electric field. The reversal of polarization can be observed by measuring the ferroelectric hysteresis as depicted by Fig.2. On increasing the electric field strength, the domains begin to align in the positive direction giving rise to a rapid increase in the polarization (OB). At very high field levels, the polarization reaches a saturation value ( $P_{sat}$ ). The polarization does not fall to zero on removal of the external field. At zero external field, some domains remain aligned in the positive direction, as a result of which the crystal will show a remnant polarization  $P_r$ . Complete depolarization of the crystal is not possible until a field of magnitude OF is applied in the negative direction. The amount of external field needed to reduce the polarization to zero is called as the coercive field strength  $E_c$ . ON increasing the field to a more negative value, the direction of polarization get flipped as a result of which a hysteresis loop is obtained. The value of spontaneous polarization  $P_s$  (OE) is obtained by extrapolating the curve onto the polarization axes (CE).



**Fig. 2: A Polarization vs. Electric Field (P-E) hysteresis loop for a typical ferroelectric crystal.**

## 1.4 Bismuth sodium titanate (BNT)

Formula:  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ . It is a widely used lead free ferroelectric material.

### Bismuth Sodium Titanate Structure

Bismuth sodium titanate is an  $\text{ABO}_3$  distorted perovskite with a rhombohedral  $R3c$  crystal structure at room temperature. The standard  $\text{ABO}_3$  perovskite formula for BNT is  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ . An  $\text{ABO}_3$  perovskite can be considered in two ways; one way is to have the bismuth and sodium cations occupy the corners of a cubic unit cell, with oxygen cations occupying the face centers thus forming octahedra, and a titanium cation in the center of the oxygen octahedra. Another way is a three-dimensional cubic network of 8 corner-sharing  $\text{TiO}_6$  octahedra with bismuth and sodium cations at the center of the cube formed by the octahedra. Figure 3 represents a typical  $\text{ABO}_3$  perovskite, shown here as cubic BNT. The figure suggests that the bismuth and sodium ions are ordered on the A-site of the structure; this is only to show the stoichiometry that is present in an ideal mixture.

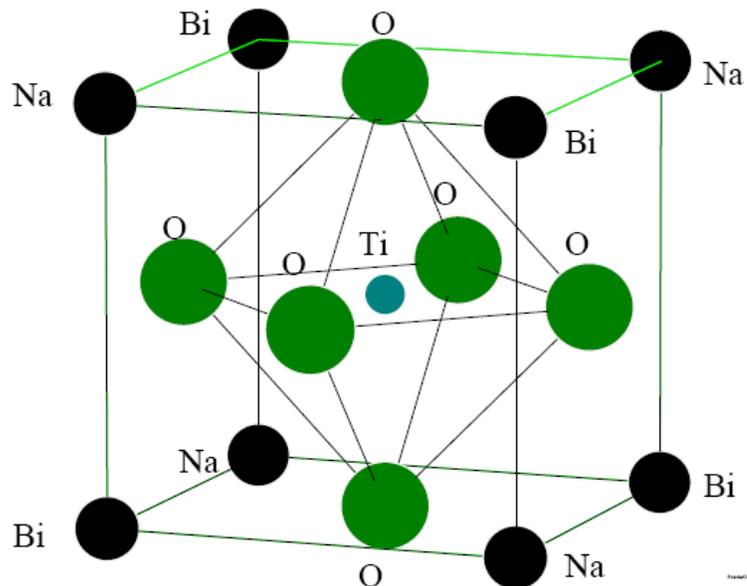
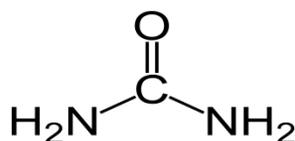


Fig 3. Representation of an  $\text{ABO}_3$  perovskite shown as cubic BNT

## 1.5 Urea

Chemical formula  $\text{CO}(\text{NH}_2)_2$ . The structure of urea is shown in the figure below:



**Fig 4. Structure of Urea**

It is used as a fuel in material science research field. It is a crystalline material that is why it has melting temperature of  $132.7^{\circ}\text{C}$ , and it diffuses before boiling.

## 1.6. Auto Combustion Technique

The solid state method is limited by its requirement for a high sintering temperature ( $>1400^{\circ}\text{C}$ ), causing Bi ion volatilization, which occurs at temperatures above  $1130^{\circ}\text{C}$  [6]. Moreover, the solid state technique produces a powder with large particle size and a wide range particle size distribution. However, the technique requires a long processing period and repeated heat treatment to obtain the desired products. The advantage of the hydrothermal technique is the capability of producing fine particle size. The stoichiometry of the products is, however, dependent on the kinetics and thermodynamics of the elements during hydrothermal reaction.

Combustion synthesis has emerged as a facile and economically viable technique for the preparation of catalysts, advanced ceramics and nanomaterials. Recent innovations in combustion and processing parameters have resulted in a better understanding of combustion phenomena and control of microstructure and property of the products.

In contrast, the soft combustion technique has the advantages of better homogeneity, lower formation temperature, a simple experimental set-up, inexpensiveness and production of fine sized powders with a narrow particle size distribution range. [7, 8]

## CHAPTER II

### LITERATURE SURVEY

#### *2.1. Why lead free..??*

The lead based materials were widely used in various industries like marine or ship applications, lead paint industry, lead battery industries which were the principle consumers of lead. Several legal sanctions are imposed on the use of lead based material due to its toxic and environment unfriendly nature.

But as we know lead based materials showed very good dielectric, piezoelectric properties it was very difficult to find a replacement for lead base. Finally researches were successful in finding lead free materials of great importance, among which BNT is most promising lead free ferroelectric ceramic.

BNT was discovered as one of the promising lead-free piezoelectrics. Sodium bismuth titanate ( $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ) is a ferroelectric ceramic having  $\text{ABO}_3$  perovskite structure of which A-site complex occupation that has been widely studied [9]. It is a good alternative to the lead base materials. Its crystal structure is rhombohedral at room temperature and changes to tetragonal at  $200^\circ\text{C}$  with the ferroelectric property dying out to give anti-ferroelectric property. At  $320^\circ\text{C}$ , the spontaneous polarization completely vanishes sweeping to paraelectric property. That is why this temperature is termed as transition temperature. With a remnant polarization ( $P_r$ ) and coercive field ( $E_c$ ) of about  $38\mu\text{C}/\text{cm}^2$  and  $73\text{ kV}/\text{cm}$ , BNT is proved to be a good ferroelectric material.

As pure BNT is difficult to be poled, hence its practical application is limited. A lot of researches are going on by doping BNT with various dopants like BNT-CT, BNT-BT, BNT-KNbO<sub>3</sub> (KN), BNT-KN, La-doped BNT [6], BNT-KNbO<sub>3</sub> (KN) solid-solution ceramics and BNT-BT compositions etc. to make viable for easy poling. Of these the modified BNT ceramics of the BNT-KN system are of the most interest because of their high potential for improvement

of the piezoelectric and dielectric properties. These problems were overcome by forming solid solutions with  $\text{BaTiO}_3$ ,  $\text{BiFeO}_3$ ,  $\text{NaNbO}_3$ ,  $\text{SrTiO}_3$ ,  $(\text{K}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ , etc. [10–15]. Among these solid solutions  $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$  system has attracted a great deal of attention owing to the existence of a rhombohedral–tetragonal morphotropic phase boundary (MPB) near  $x = 0.06$ – $0.08$ , where the materials show significantly enhanced piezoelectric properties and reduced coercive field.

Dopant segregated cation vacancies as well as acceptor solutes at the grain boundaries are used to induce the space-charge region [16], thereby inhibiting grain growth. Some electrical properties such as piezoelectric coefficient, dielectric properties and loss tangent can also be enhanced by tuning the concentration of the dopant. There is very little information on the effects of dopants on BNT. However, considerable research carried out on doping of other lead-free compounds can provide useful guidance.  $\text{CuO}$ ,  $\text{MnO}$ ,  $\text{MnO}_2$  and  $\text{ZnO}$  have been doped into piezoelectric compounds to reduce sintering temperature and improve electrical properties of the compounds [17, 18].  $\text{CuO}$  doping has proven beneficial to improve densification of the product.  $\text{Mn}$  doping in BNT has been found to decrease phase transition temperature and to increase the values of electromechanical coupling factors and the piezoelectric constant  $d_{33}$ .

BNT can be synthesized in many routes like solid state synthesis, chemical method and many other techniques. Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, inexpensive method for the production of various industrially useful materials. In the current times, CS has become a very popular approach for the preparation of nanomaterials and is practiced in nearly 65 countries. A number of important recent breakthroughs in this field have been made, significantly for the development of new catalysts and nano carriers with properties better than those for similar traditional materials. Extensive research carried out in last five years has emphasized the SHS capabilities for improvement of materials, energy saving and environmental protection. The significance of industrialization of the SHS process has also been realized. It is an easy and convenient method for the preparation of a variety of advanced ceramics, catalysts and nanomaterials. In this technique, on the basis of the principles of the propellant chemistry, a thermally induced redox reaction takes place between a fuel and an oxidant. Many types of

combustion synthesis exist which differ mainly in the physical state of the reactants or in the combustion modality [19, 20–25]. By combustion-based methods, monophasic nano-powders with homogeneous microstructure can be produced, at shorter reaction times or lower temperatures, compared to other conventional methods like solid-state synthesis or nitrate method. Citrate–nitrate auto-combustion synthesis (CNA) is a very popular solution combustion method, where the fuel is citric acid and metal nitrates are used as metal and oxidant source. The CNA method shows notable similarities with the very well-known Pechini process [26, 27] and it can be more properly described as a “sol–gel combustion method”.

Urea and starch are also being used as fuel in the synthesis of  $\text{Al}_2\text{O}_3\text{--ZrO}_2$  nanocomposite powder by solution combustion process. A thermodynamic modeling was used to theoretically predict the effect of fuel composition on the exothermicity of the combustion synthesis process. Fuel and fuel-to-oxidant ratio plays a very important role in determining the properties of the synthesized products like crystallite size, morphology, phases, degree specific surface area, and nature of agglomeration. Urea used as a fuel yields powders with low specific surface area and hard agglomerates, owing to the formation of stable polymeric intermediates that prevent the dissipation of heat and thereby sintering the oxides during combustion.

It has been also reported that the synthesis of  $\alpha$ -alumina-t-ZrO<sub>2</sub> (ZTA) nanoceramic powders through solution combustion technique by employing a novel mixture of ammonium acetate, urea and starch as fuels. As Starch has big molecules made up of glucose repeat units, hence it has a large heat of formation. Therefore replacing starch with a part of urea in the fuel mixture will reduce the exothermicity of the combustion reaction, with the release of almost equal number of mole gases in comparison with pure urea in the reaction with nitrates as oxidizer. In general, a good fuel used in a combustion process should react non-violently, release non-toxic gases, and behave as a complexant for metal cations.

## 2.2 Thesis Objective:

- To synthesize the lead-free ferroelectric material ( $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ) by auto-combustion technique.
- To reduce the processing (calcination) temperature.
- To characterize the synthesized lead free ferroelectric material ( $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ) by X-Ray Diffraction for phase formation, Scanning Electron Microscopy for surface morphology and electrical study for dielectric and ferroelectric property.

## CHAPTER III

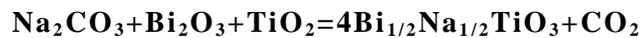
### EXPERIMENTAL WORK

#### 3.1 Introduction to sample synthesis

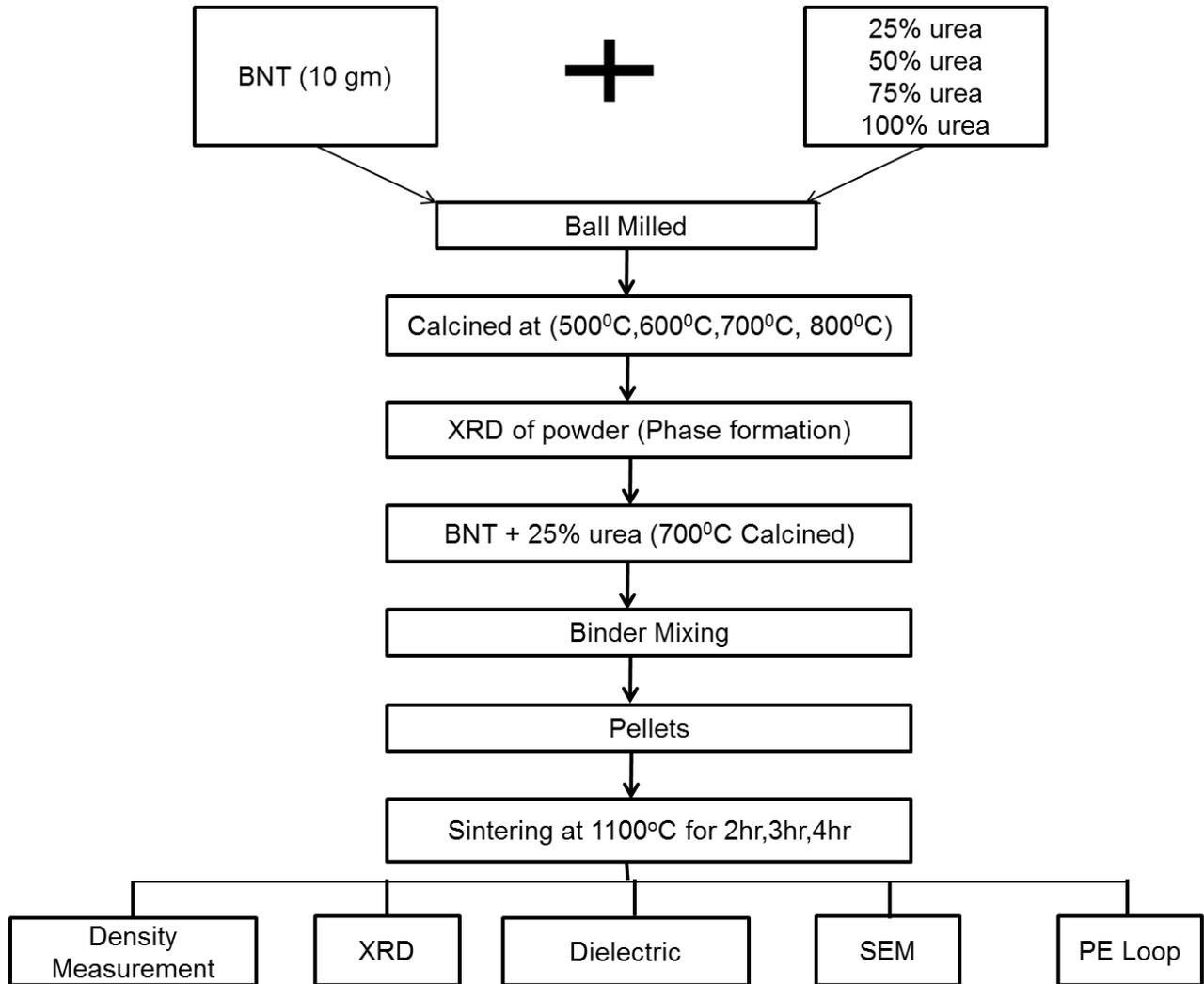
In this chapter, the synthesis and characterizations for preparation of BNT ( $\text{Bi}_{0.5}\text{Na}_{0.5}$ )  $\text{TiO}_3$  ferroelectric ceramics are discussed in details:

The precursors used are:  $\text{Bi}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{TiO}_2$ . The stoichiometric amount of precursors was taken for synthesis of 10g of BNT. The precursors amount was calculated by atomic ratio calculation, as follows  $\text{Na}_2\text{CO}_3 = 1.2506\text{g}$ ,  $\text{Bi}_2\text{O}_3 = 5.4976\text{g}$ ,  $\text{TiO}_2 = 3.7768\text{g}$  were taken and grinded for 2hrs and then ball milled for around 12 hrs in acetone medium for complete mixing of the precursors. Along with precursor, urea as a fuel was taken in different proportions like 25wt%, 50wt%, 75wt%, 100wt%, and ball milled in acetone medium using zirconia balls as grinding medium for complete mixing of precursors as well as the urea in the precursor. After ball milling, the samples were kept for some days till the acetone evaporated and it got dried. Then the powders were removed from the bottle and grinded for around 4hrs till the powders became fine.

The chemical reaction involved is



**3.2 Flowchart for synthesis of BNT ceramics**



**Fig.5: Flowchart of synthesis procedure**

### **3.3 Synthesis techniques**

#### **3.3.1 Auto combustion method**

Combustion synthesis (CS) or self-propagating high temperature synthesis (SHS) is an effective, low cost method for production. It was concluded that the conventional Solid State SHS being a gasless combustion process typically yield much coarser particles than solution combustion approach.

In this work of urea was chosen as the fuel, which act as a self-catalyst and generates heat as its melting point is very low ultimately it helps in increasing the reactivity of the samples yielding a good result as compared to solid state process.

#### **3.3.2 Ball Mill**

A ball mill is an efficient technique for grinding of very fine particles. It is widely used in various industries like chemical industries and ceramic industries.

A conventional ball mill consists of rotating drum half filled with steel balls. As the drum rotates, the balls drop on the precursors (ceramic powders) that are being ground; the rate of grinding increases with the speed of rotation. At high speeds, the centrifugal force acting on the steel balls exceeds the gravitational force, and the balls are pinned to the wall of the drum. At this point, the grinding action ceases. We can also use other materials as grinding media including flint pebbles, ceramic balls and stainless steel balls.

#### **3.3.3 Calcination**

The well grinded powders were taken in an alumina crucible for calcination in a Bysakh made okay furnace at different temperatures 600°C, 700°C and 800°C for 4hrs at rate of 5°C per minute rise. It is a thermal treatment process applied to ores and other materials in order to bring about a thermal decomposition phase transition or removal of a volatile fraction.

1. It is a heat treatment process which promotes diffusion.
2. The purpose is to drive off  $M_2O$ ,  $SO_2$ ,  $CO_2$  and other volatile substances.

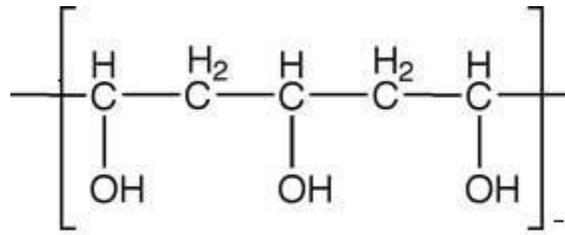
- Temperature of calcination must be less than the temperature of melting of the materials, which differs from materials to materials.

$$T_{\text{calcination}} < T_{\text{melting point}}$$

At  $T_{\text{calcination}}$  Gibb's free energy is Zero. It influences density and electromechanical property of final product, inter diffusion of ions of the constituents, and phase transition. Greater  $T_{\text{cal}}$  suggests greater homogeneity of the final product, as it can be heated to a greater extent.

### 3.3.4 Binder Mixer

Poly Vinyl Acetate is a water soluble binder and is manufactured by hydrolysis of Poly Vinyl Acetate (PVA) in presence of a catalyst. 5% aqueous solution of PVA was added with the calcined powders and grinded for few times then left it to get dry. After the powder gets dried it was again grinded for around 30 min till we get fine powders.



**Fig. 6 Molecular structure of PVA**

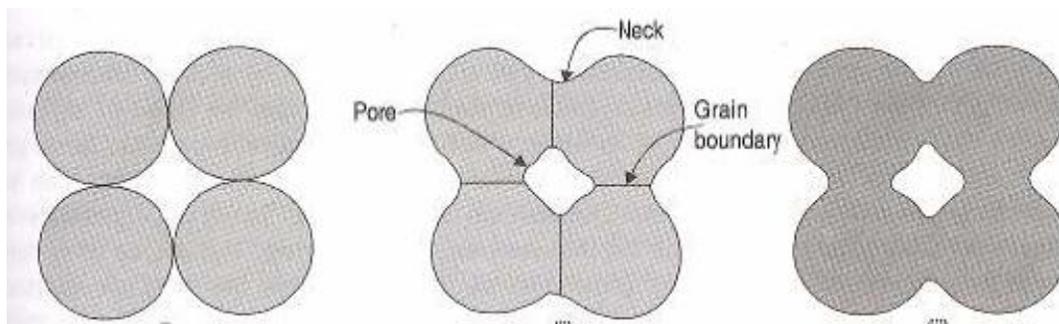
It has C-C linkage and the -OH groups provide initial wetting and adhesion properties. PVA is largely used as a binder in dry pressed ceramics as it provides better mechanical stability to green bodies. Binders provide better green strength to the ceramic bodies and their efficient removal from the system during sintering plays a crucial role in bulk density and strength of sintered bodies.

### 3.3.5 Sintering

Density of the electronic ceramic is a very sensitive parameter and that directly affects their properties. Therefore, proper sintering of the pellets is essential for electrical measurement. The pellets were taken on an alumina plate and sintered at different temperatures in Bysakh made Okay furnace at a heating rate of 5°C per minute at 600°C, 700°C, and 800°C for volatile fraction removal if any in the initial heat treatment.

It is the process of consolidation of either loose aggregate of powder or a green compact of the desired composition under controlled conditions of temperature and time.

Densification occurs during sintering and solid state sintering is carried out at temperatures where material transport due to diffusion is appreciable. Atomic diffusion is required, since surface diffusion is required. In between the granules, a small granule is present, when pressured the surface area increases and the material gets densified. Densification process is shown in fig 7 below.



**Fig. 7: Densification process**

### 3.3.6 Density Measurement:

After heat treatment of the samples, the dry weights of the pellets were measured by a digital electronic balance. Following this, the samples were given different identification to avoid any confusion and kept together in a glass beaker containing kerosene. The samples containing beaker was kept in desiccator for around 45 minutes and simultaneously vacuum was also

created by the use of a suction pump. Then it was observed till the arising of bubbles form the beaker in the desiccator stops. The suction pump used for creating vacuum was switched off and the vacuum was slowly released. Now the beaker was taken out of the desiccator. The weight of the pellets was measured, by suspending the pellets in the beaker containing kerosene with the help of a bench, and special designed hanger, to hang the pellets in the kerosene. And the measurement was done in a digital electronic balance. This measurement is represented as suspended weight .after the suspended measurement the pellets were removed from the beaker and dried using a filter paper in order to remove the kerosene content on the surface of the pellets. This measurement was done using the digital electronic balance and interpreted as soaked weight. The experimental bulk density and apparent porosity were measured by using Archimedes principle:

$$\text{Bulk Density} = D / (W-I)$$

$$\text{Apparent Porosity} = (W-D) / (W-I)$$

Where:

*D*-Dry weight,

*W*-Shocked weight

*I*-Suspended weight.

### 3.4 Characterization Techniques

#### 3.4.1 XRD

X-Ray Diffraction (XRD) technique is a powerful tool for material characterization as well as for detailed structural elucidation. As the physical properties of solids (e.g., electrical, magnetic, ferroelectric, optical, etc.) depend on atomic arrangements of materials, therefore the determination of the crystal structure is an indispensable part of the characterization of materials, chiefly the identification of the chemical species.

X-Ray Diffraction patterns are used to establish the atomic arrangement or structure of the materials because the d spacing of diffraction planes is of the order of X-Ray wavelength  $\lambda$ , the various orders  $n$  of reflection occur only at the precise values of angle  $\theta$ , which satisfies the Bragg equation given by  $n\lambda = 2d\sin\theta$ .

The powder profile of a substance can be used for identification of materials, even without any further interpretation.

The accurate determination of lattice parameters provides an important basis in understanding various properties of the materials. The lattice parameters from the line positions or d-spacing can be calculated from *CHECK CELL*.

The kinematics theory of X-Ray diffraction describes that for a perfect cause, the spread in the intensity distribution curves, the nature and extent of the intensity spread is an obvious measure of crystal imperfection present in the sample. The different types of defects may be co-existent in crystalline materials; hence the problems that arise are of separation of different types of defects and identification and quantitative estimation of the extent and distribution of each type of defect. The various factors affecting the diffraction intensities can be grouped into a single expression for use in calculating the relative intensities of reflections. X-Ray diffraction is an important technique in material characterization. It is useful for both powder as well as pellet analysis.

In the present case, calcined powders were characterized with respect to phase quantity measurement, phase identification, crystallite size determination, quantity measurement and lattice parameter measurement, etc., by using Cu-K $\alpha$  XRD (X-pert MPD, Philips, UK). For quantitative estimation of phases, calcined powders were first uniformly mixed, and then the resulting mixture was analyzed with the help of a step size of  $2^\circ/min$ . The relative weight fractions were quantified from the ratio of peak areas. The phases that gave maximum peak area at a particular temperature were considered as 100% formation of those phases at that temperature. XRD of sintered samples were also analyzed.

Considering that area as 100%, the relative percentages of the respective phases were calculated. And the lattice parameters of the sintered pellets were calculated using *CHECK CELL*.

### 3.4.2 Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) is a useful technique to study the topography and morphology of the materials with much higher resolution. The working principle of SEM is that when a beam of highly energetic electrons strikes the sample, the secondary electrons, x-rays and back-scattered electrons are ejected from the sample. These electrons are then collected by the detector and convert into signal that displays on a screen.. This wide spread use of electron microscopes is based on the fact that they permit the observation and characterization of materials on a nanometer (nm) to micrometer ( $\mu\text{m}$ ) scale. It is widely used by the researchers in order to get

- Topography: Information about the surface of the object.
- Morphology: The size and shape of the particles making the object.

In the present study, the SEM micrograph was taken on the fractured surface of the sample using scanning electron microscope (SEM: JSM-840 scanning microscope JEOL).The samples were made conducting by coating a thin layer of platinum using a sputter coater. For the measurement of grain size, lines of known length were drawn on the micrograph. The number of grains that were cut by the lines was counted. The average grain sizes were then calculated by dividing the length of the line by the number of grains coming under that line. A minimum of 10 lines, each of length not less than 200 micrometers were drawn on the different places of a single micrograph and average grain sizes were calculated to minimize the error.

### 3.4.3 Dielectric Measurement

To measure the relative permittivity (dielectric constant) and dielectric loss, LCR meter can be used. In this work, LCR Tester (Hioki, Japan, 42Hz – 1MHz) were used to measure the dielectric constant and dielectric loss at a desired frequencies with varying temperature range. The dielectric constant nearby phase transition temperature can be obtained from this study as well as the contribution of different polarization towards the dielectric property of the material at

different temperatures and frequencies. The nature of the material be it relaxor or normal ferroelectric, can also be detected by studying at different frequencies. The pellets were made conducting by coating with silver paste for the dielectric measurement. The measurements were done in the LCR meter temperature range ranging from room temperature to 400<sup>0</sup>C at 3<sup>0</sup>C per minute. And the data was taken for four different frequencies 1k,10k,100k,1MHz. The LCR meter, was interfaced with the computer and the data (capacitance and *D* factor) was collected as a function of temperature. The measured capacitance was then converted into dielectric constant using the following formula:

$$C = \epsilon_0 \epsilon_r \frac{A}{d}$$

$$\epsilon_r = \frac{C \times d}{\epsilon_0 \times A}$$

Where,

*C* : Capacitance in farad (*F*)

$\epsilon$  : Permittivity of free space in farad per meter ( $8.85 \times 10^{-12} F/m$ )

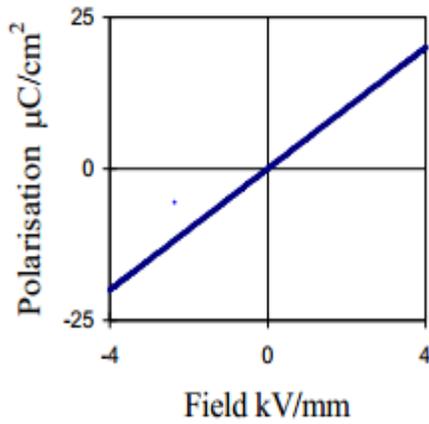
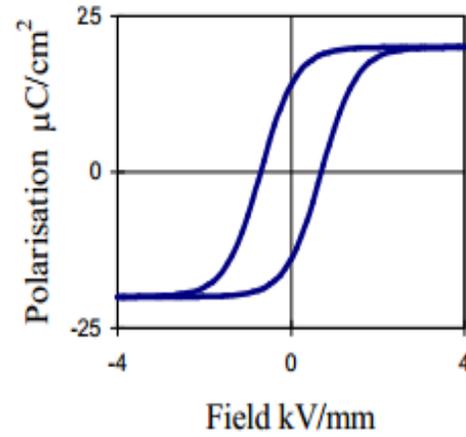
$\epsilon_r$ : Dielectric constant or relative permittivity of the sample.

*A*: Area of each plane electrode in square meters ( $m^2$ )

*d*: Separation between the electrodes in meters (*m*)

### 3.4.4 Hysteresis Measurement

The hysteresis measurement is done to confirm the ferroelectric property of the material. A P-E loop tracer shows a plot of the polarization (*P*) versus applied ac field to (*E*) at a given frequency. The spontaneous polarization (*P*<sub>s</sub>), remnant polarization (*P*<sub>r</sub>) and the coercive field (*E*<sub>c</sub>) can be measured by studying the hysteresis loop.

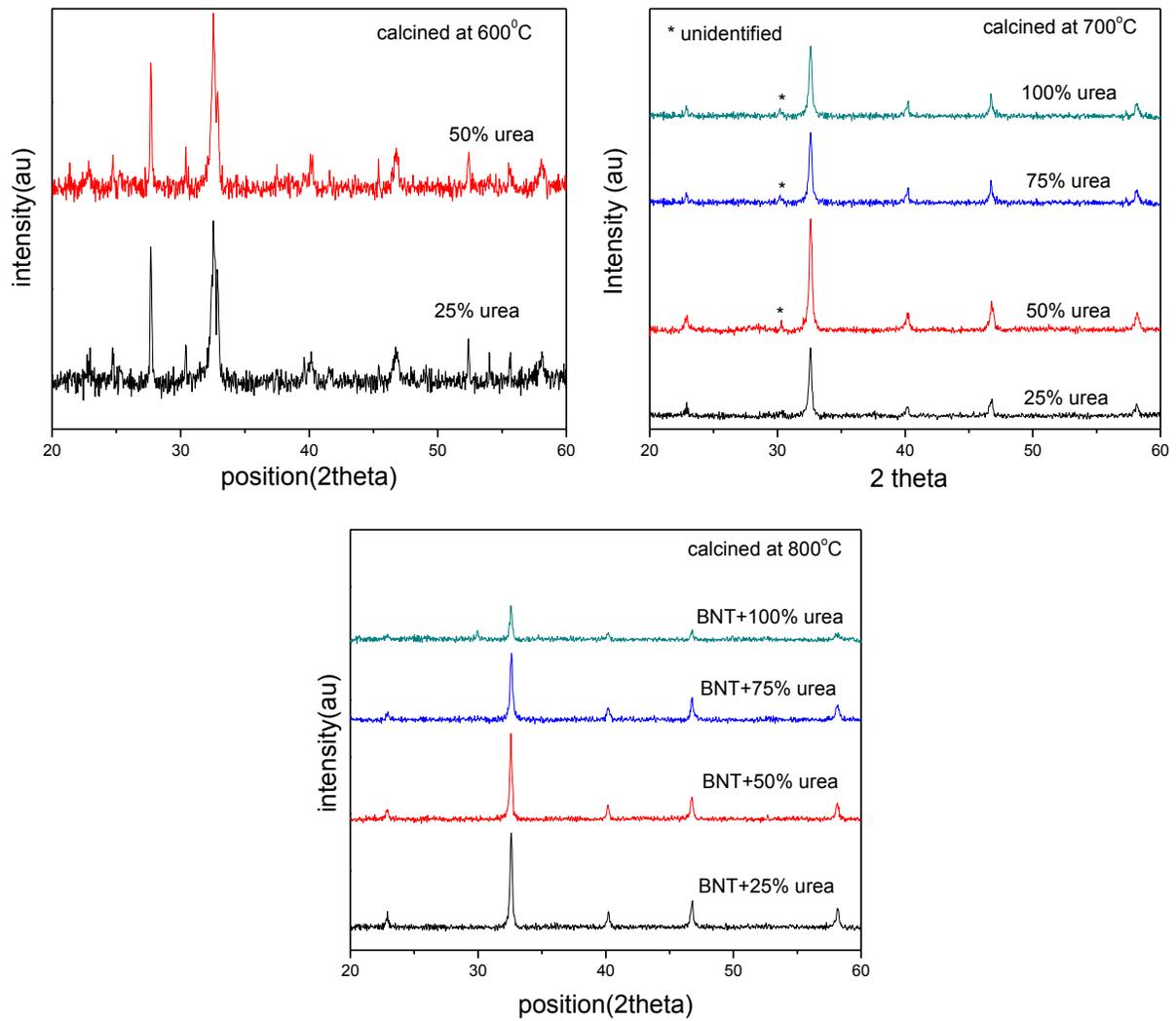
**Fig 8: Lossy capacitor response****Fig.9: Non-Linear ferroelectric response**

From figure 8, we observe that the area within the loop is proportional to the loss tangent of the device, and the slope is proportional to the capacitance. If we consider less ideal devices such as non-linear ferroelectric materials we would get a P-E loop such as figure 9, where the loss is less. In this work, for the polarization with different fields, it was studied using the Radiant technology P-E loop tracer. Various data were measured at 100 ms for different voltages from 10kV to 75kV.

## CHAPTER IV

### RESULTS & DISCUSSION

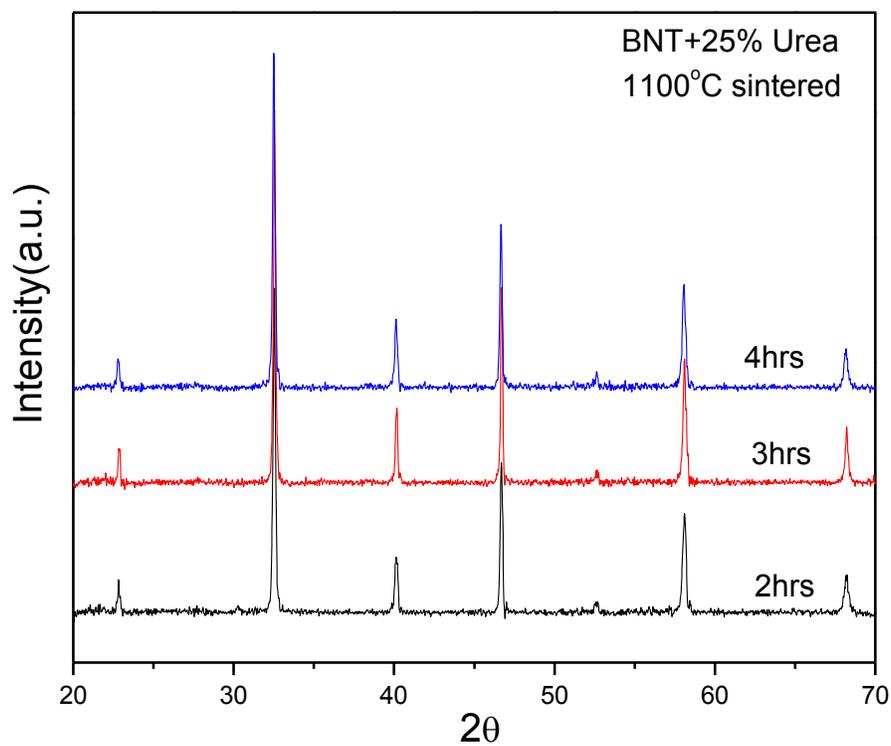
#### 4.1 XRD Analysis



**Fig. 10: XRD of powder (intensity vs. position)**

Fig10 shows the XRD pattern of calcined BNT powders in different fuel concentrations at different temperatures. Fig.10 (a) confirms the formation of BNT phase at 600°C itself with some impurities. Further increasing the calcination temperature, the impurities get minimized and show the pure BNT phase at 700°C and 800°C. Compare to the higher fuel concentrations (50 and above wt% of urea), the lower fuel concentration (25wt% of urea) shows the proper pure at 700°C. This may be due to the fact that the uniformity of oxide mixture varies with the variation of urea ratio [28]. At 800°C of higher fuel concentration shows the pure phase, but our objective is to reduce the processing temperature of BNT system. Whereas, in the same system synthesized by solid state reaction route single perovskite phase developed at above 900°C [29]. Finally, we have chosen the 25wt% urea sample calcined at 700°C for subsequent preparation. The basic principle of reduction of processing temperature by using fuel is that when an organic compound combusts within a mixture, it gives releases heat that can be effectively supplied to the raw powders in the mixture. The energy supplied in this way accelerates the chemical reaction between raw powders and also reduces the reaction temperature [30].

The pellets have been prepared from the BNT + urea 25wt% sample calcined at 700°C and sintered at 1100°C for different duration (2, 3 and 4hrs). Fig.11 shows the XRD pattern of sintered BNT pellets at 1100°C for 2, 3 and 4hrs. The XRD analysis of the sintered pellets shows that the samples (BNT) are single phase and the monoclinic structure with space group P2/m. The observed patterns have been indexed using standard pattern JCPDS no. 46-0001. The lattice parameters have calculated using a computer programming “CHECKCELL” and the values are tabulated in Table.1.

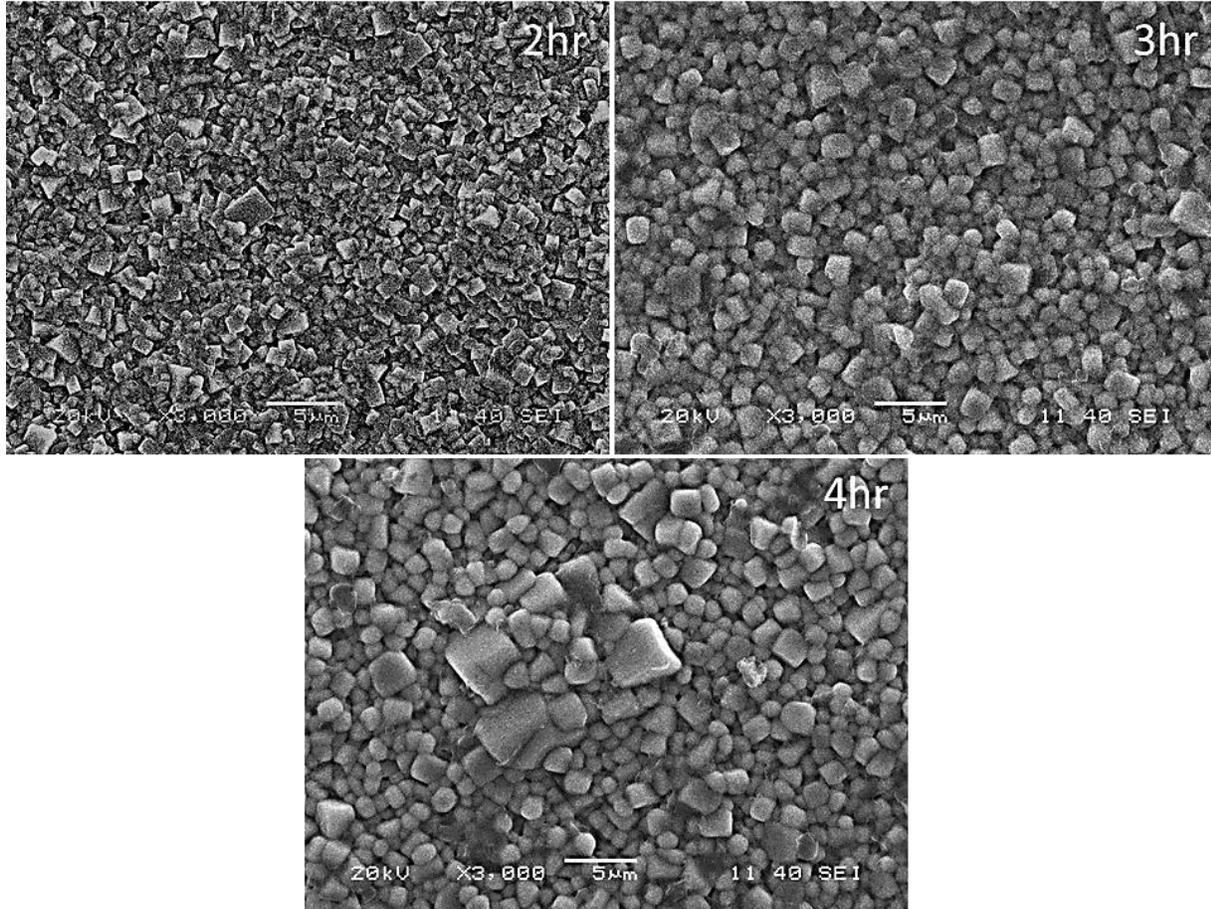


**Fig. 11: XRD of pellet**

**Table.1**

	2hr	3hr	4hr
a	5.5151 (6)	5.5289(2)	5.5093(7)
b	6.7159(10)	6.6968(4)	6.7332(10)
C	5.5006(5)	5.5115(3)	5.5077(5)
Volume	176.16	176.26	176.70

## 4.2 SEM Analysis

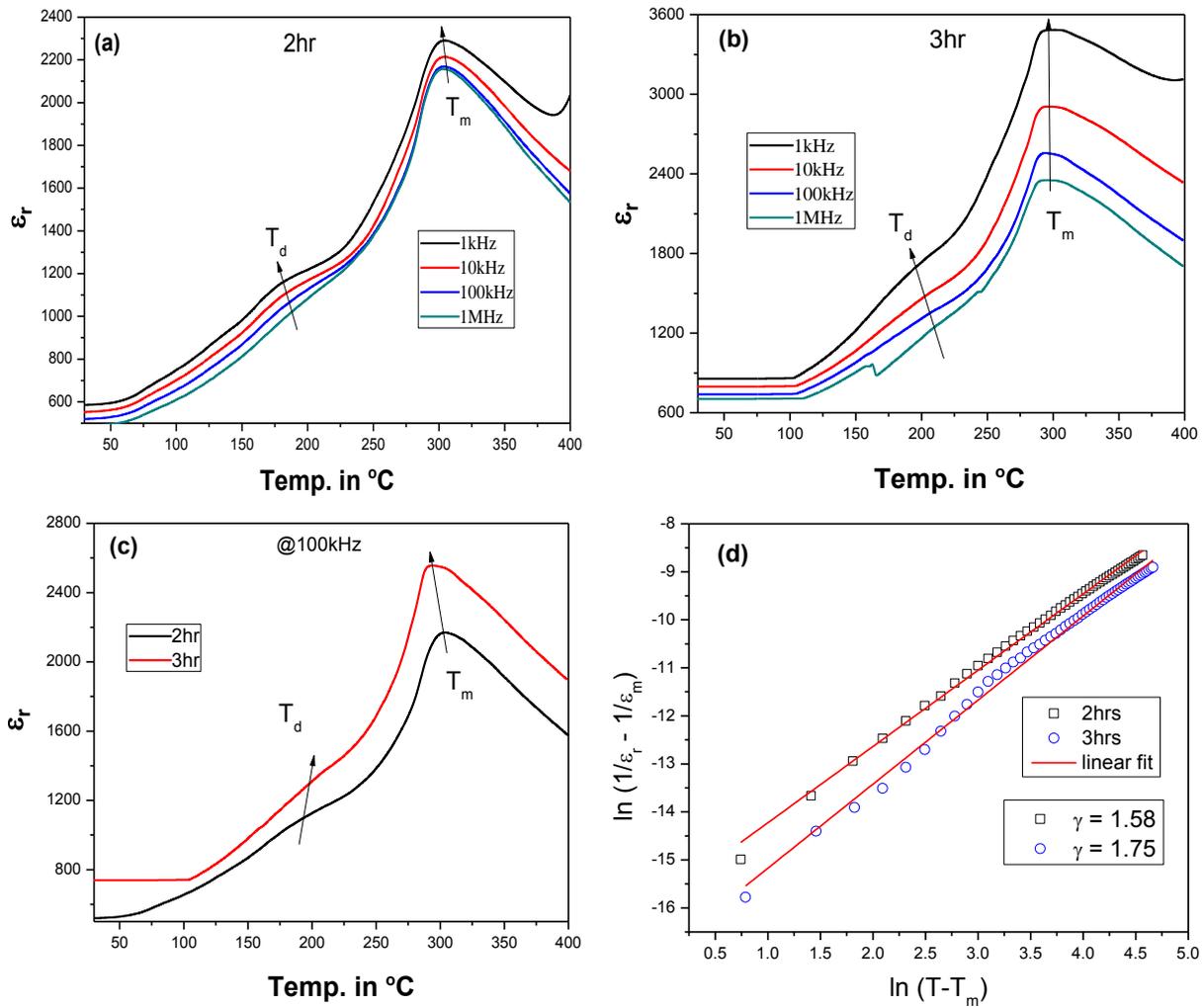


**Fig12: SEM micrograph**

Fig.12 shows the SEM micrograph of sintered pellets at 1100°C for different duration (2, 3 and 4hrs). The SEM micrographs show the polycrystalline nature of the sample with a nearly rectangular grain of different sizes, non-uniformly distributed throughout the sample surface. The grains and grain boundaries are found to be well-defined and clearly visible. The grain size significantly increases by increasing the sintered temperature which enhances the grain growth. It was found that the average grain size of the sintered BNT ceramics at 1100°C for 2, 3 and 4 hrs are ~1.16, 1.43 and 1.83µm respectively. The densities of sintered ceramics at 1100°C for

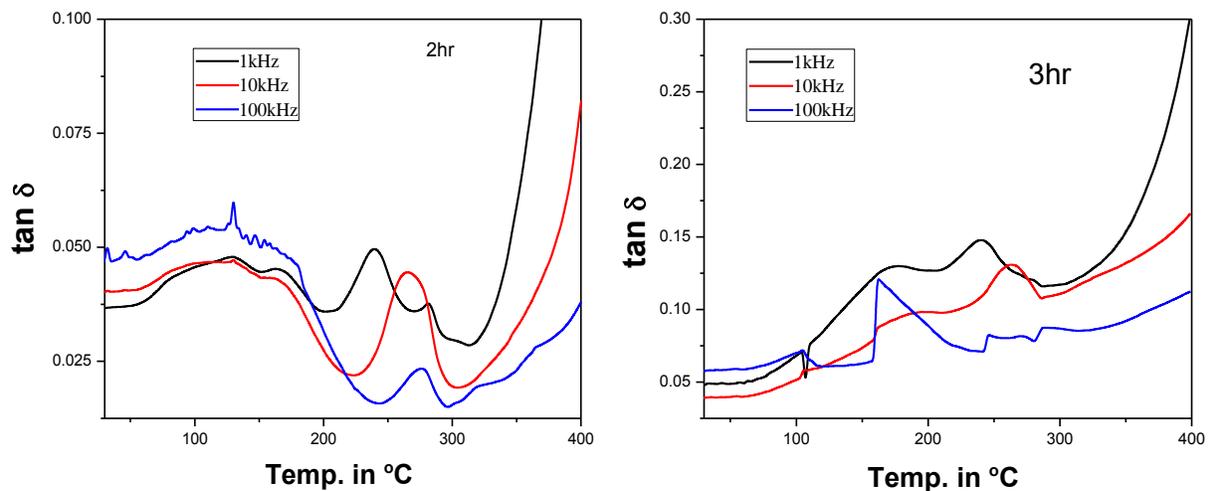
different durations are about ~93% of the theoretical density, which is in the similar range of that found in Herabut and Safari [31] of between 93% and 95% and Nagata and Takenaka[32] of more than 90%.

### 4.3 Dielectric Study



**Fig13: Dielectric constant plot with temperature**

Temperature dependence of relative dielectric constant at measuring frequencies of 1 kHz, 10 kHz, 100 kHz and 1 MHz is shown in figure 13. It can be seen from figure that the phase transformation process of BNT is complex. The dielectric constant increases with increase in temperature, attains its maximum value ( $\epsilon_{\max}$ ) at maximum temperature ( $T_m$ ) and then decreases. There are two  $\epsilon_r$  peaks in the graph, which appear at 192 & 200 (marked by  $T_d$ ) and 303 & 293°C (marked by  $T_m$ ) for 2 and 3 hrs sintered sample, respectively, and we call these two temperatures as characteristic temperature (abbreviated as  $T_c$ ). The conventional explanation, regarding this phenomenon, is that different phase transformation processes occur at two  $T_c$ ; ferroelectric–anti-ferroelectric transformation process at around 200°C and anti-ferroelectric–paraelectric transformation process at around 300°C [33]. Our observed variations of dielectric constant with temperature at different frequencies are analogous with the report by Kim *et al* [34].

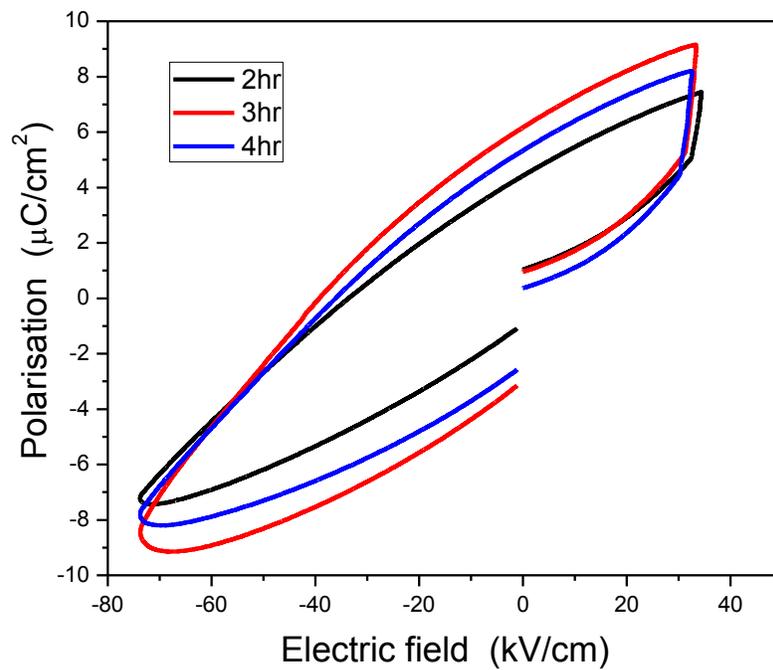


**Fig14: Tangent loss with temperature**

Figure 14 shows the variation of  $\tan \delta$  with temperature at different frequencies. It can be observed that the tangent loss ( $\tan \delta$ ) increases with increase in temperature at all frequencies. The small increase in the value of  $\tan \delta$  of BNT is up to 330°C, and above this temperature there is a sudden increase in  $\tan \delta$  on further increase in temperature. The increasing trend in  $\tan \delta$  at the higher temperature region (for all frequencies) may be due to space charge polarization [35].

#### 4.4 Polarization Vs. Electric field study:

Figure 15 shows the polarization vs. electric field curves for samples sintered for various durations. A nature of the loop confirms the ferroelectric nature. On increasing the sintering durations, the saturated polarization increases from 2 to 3 hrs and then decreases for 4 hrs sintered samples. As per the morphology study, grain size in the 2 and 4hrs sintered pellets show the inhomogeneous nature, which decreases the polarization and 3 hrs sintered pellet shows the homogeneous nature which shows high polarization property.



**Fig15: Hysteresis loop**

**Table.2**

Applied field 75kv	Maximum Pr	Pr ( $\mu\text{C}/\text{cm}^2$ )	Ec (kv/cm)
2hr	7.43641	4.4204	3.498
3hr	9.1398	6.16297	4.159
4hr	8.0908	5.3314	3.827

## CONCLUSION

BNT was successfully prepared by auto-combustion route. Results came good with powder synthesized at 700°C with 50wt%. Calcination temperature seen to be reduced significantly which is a good outcome of combustion route. Urea as fuel was well dispersed throughout the powder provided thermal energy at local region for reducing the particle size. Sintering duration affected a lot in controlling the grain growth. Pellet sintered for 3hr was observed to have homogeneous grain and less porous morphology. The dielectric and ferroelectric property were seen improved marginally for this cause.

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