

# SYNTHESIS OF LOW LOSS LEAD FREE PIEZOELECTRIC BNT-BT CERAMIC

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By

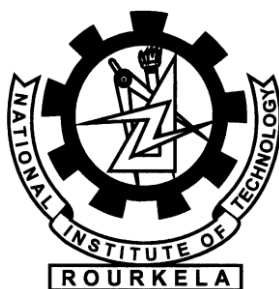
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## **National Institute of Technology**

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## **CERTIFICATE**

This is to certify that the thesis entitled “**Synthesis of low loss lead free piezoelectric BNT-BT ceramic**” submitted by Mr. **Chinmayaranjan Moharana** in partial fulfillment of the requirements for the award of **Bachelor of Technology Degree in Ceramic Engineering** 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 thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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## **Abstract**

Oxide materials with perovskite structure having the general formula  $ABO_3$ , form the backbone of the ferroelectrics industry. For a long time, ferroelectric materials have come into widespread use in applications that range in sophistication from medical ultrasound and underwater sonar systems, smoke detector buzzers to novel applications in active and passive damping systems for sporting goods and automobile and aerospace sectors. However, an attention has been focused across the globe to find out new environment-friendly lead-free ferroelectric materials. The  $(Bi_{0.5}Na_{0.5})TiO_3$  (BNT) based composition is reported as the promising for piezoelectric applications. Application of BNT into practical devices has been hindered by leakage problems that lead to low resistivity. In order to reduce the problems mentioned here, the method of forming binary solid solutions with other perovskites with good dielectric properties was adopted.

The present work deals with the synthesis, densification and characterization of  $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$  (BNT)-  $x BaTiO_3$ (BT) solid solution (where  $x=0, 0.06$ ). Solid state synthesis method and autocombustion technique have been adopted to synthesize phase pure powder. Phase pure BNT- BT powder can be prepared at a temperature as low as  $600^\circ C$  by auto-combustion route. It is very difficult to prepare phase pure solid solution system by conventional solid state synthesis method. 96% of theoretical density was achieved for combustion synthesized powder.

## CHAPTER-1

### INTRODUCTION

#### **Bismuth Sodium Titanate**

The Bismuth Sodium Titanate (BNT) family of dielectric materials is a relatively new family of dielectrics. It is being studied because of its high dielectric constant, as well as its ability to work well without the addition of lead. BNT is a candidate material for future dielectric and piezoelectric applications that cover large temperature ranges. The large temperature range is advantageous for use in the oil and natural gas industry for down-hole drilling tools, automotive, aerospace and military for applications directly on or near hot engine surfaces. BNT is being studied to create a material that could someday replace the current industry standard, barium titanate or PZT.

Barium titanate (BT) is currently the most widely used dielectric material for capacitors. The various dopants that are available for the modification of BT make it the material of choice for many dielectric applications. The downside of BT is that the Curie temperature ( $T_c$ ) is only  $130^\circ\text{C}$  without the addition of lead. Lead additions increase the Curie temperature up to about  $150^\circ\text{C}$ ; however, lead also de-stabilizes the low temperature phase transitions. Above the  $T_c$ , the dielectric constant exhibits Curie-Weiss behaviour. The Curie-Weiss law, given describes the rapid decrease in relative permittivity above the Curie temperature. The drastic drop in relative permittivity beyond the Curie temperature limits the design parameters of ferroelectrics for use in high temperature applications.

$$\epsilon_r = C/T - T_0$$

Where: C is a constant for a given material (Curie Constant).

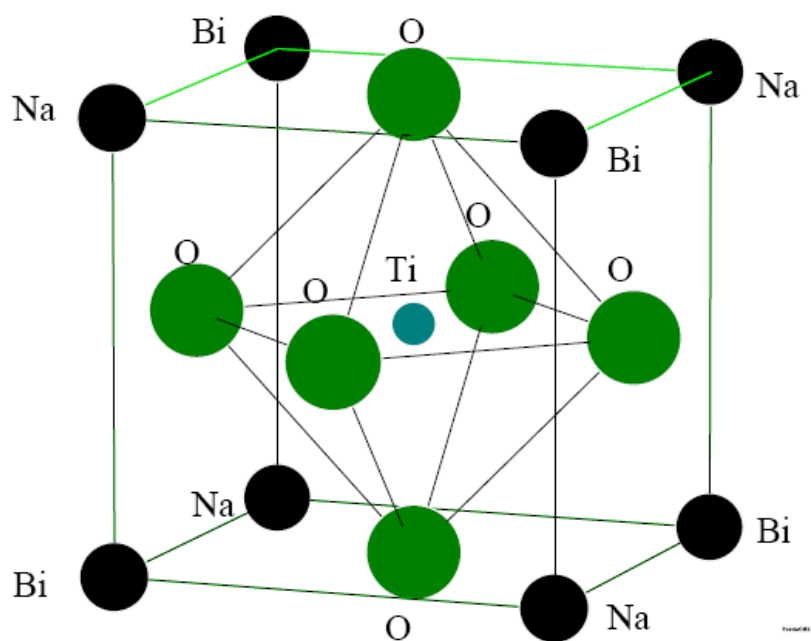
$T_0$  is a temperature near, but lower than the Curie Weiss temperature

#### **Bismuth Sodium Titanate Structure**

Bismuth sodium titanate is an  $\text{ABO}_3$  distorted perovskite with an rhombohedral  $R3c$  crystal structure at room temperature.<sup>4</sup> 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, oxygen cations occupying the face centers, and a titanium cation in the center of the oxygen octahedra that is formed. The other way, is a three-dimensional cubic network of 8 corner-sharing  $\text{TiO}_6$  octahedra with bismuth and sodium cations at the center of the cube formed by the octahedra.<sup>5</sup> Figure 1 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. The real material does not exhibit any long range ordering as described later in the text.

Many structural investigations have been performed on BNT since it was discovered in 1960 by Smolenskii et al. These studies used the best methods of the time to determine the phases and phase transitions of BNT. Phase transitions determined from these earlier studies have since been clarified by an extensive neutron powder diffraction study of BNT. This study definitively determined the phase transitions and crystal structures at various temperatures (Jones and Thomas, 2002). The results of this study are shown in Table I. As the table shows, with decreasing temperature, BNT transforms from cubic  $\text{Pm}\bar{3}\text{m}$  to tetragonal  $\text{P4bm}$  and then to rhombohedral  $\text{R}\bar{3}\text{c}$  with coexistence regions between them. These phase transitions are important to the electrical properties of the material because only non-centrosymmetric space groups can exhibit ferroelectricity



### Representation of an ABO<sub>3</sub> perovskite shown as cubic BNT

The rhombohedral R3c space group is polar with parallel cation displacements along the [111]<sub>p</sub> pseudocubic direction along with antiphase a-a-a- oxygen octahedral rotations. Thorough explanations of the types of octahedral tilting and the associated mechanisms are available to more fully understand this phenomenon (Woodward 1997). Cation displacements along with octahedral rotations allow the crystal to have a spontaneous polarization (P<sub>s</sub>); polarization is necessary for a material to be ferroelectrically active.

The tetragonal P4bm phase is also a polar phase, although it has a weaker polarization response than the R3c phase. The oxygen octahedra in the tetragonal phase exhibits a<sup>0</sup>a<sup>0</sup>a<sup>-</sup> rotation behavior about the c axis with anti-parallel cation displacements of A-site cations along the polar c-axis. The tetragonal phase distortion produces a weaker polarization response because the atomic displacements are less than those in the R3c phase. Smaller atomic displacements result in a lower polarization in the material. This is evident by the decrease in relative permittivity above the Curie temperature (320°C).

Temperature (°C)	Phase(s)	Lattice Parameters (angstroms)	Glazer Tilt System
-268 to 255	Rhombohedral – R3c	a <sub>H</sub> = 5.4887 (2) c <sub>H</sub> = 13.5048	a <sup>-</sup> a <sup>-</sup> a <sup>-</sup>
255 to 400	Coexisting Rhombohedral/Tetragonal	Variable	Mixture
400 to 500	Tetragonal – P4bm	a <sub>T</sub> = 5.5179 (2) c <sub>T</sub> = 3.9073	a <sup>0</sup> a <sup>0</sup> a <sup>-</sup>
500 to 540	Coexisting Tetragonal/Cubic	Variable	Mixture
Above 540	Cubic Prototype – Pm3m	a <sub>C</sub> = 3.91368 (3)	None

Phase transitions in ferroelectric materials are one of the main parameters that need to be controlled to tailor the properties to meet specific applications. Phase transitions are one of the main determinants of the dielectric properties of the material. Compositional additions to the BNT structure can be chosen to modify the phase transitions that occur within the material at various temperatures. Dopants are selected to change specific characteristics of the phases such as relative permittivity, Curie temperature ( $T_c$ ), relative permittivity peak height and number of phase transitions. The Curie temperature is the temperature where the relative permittivity of the material is the largest. This usually occurs where there is a phase transition. Some materials, such as  $\text{BaTiO}_3$ , exhibit Curie Weiss behavior as discussed before, while others undergo a diffuse phase transition.

Bismuth sodium titanate is a relaxor ferroelectric in the rhombohedral phase and it exhibits diffuse phase transitions between each of the phases. Diffuse phase transitions are described by a coexistence region between phases as discussed above. Diffuse phase transitions are evident in the dielectric response because the relative permittivity peaks become broad instead of having a sharp peak, like those seen in materials with Curie Weiss behavior. Broad relative permittivity peaks are most prominent in solid solutions and in disordered structures. The Curie range, rather than the Curie temperature can be used to describe the broad peaks that are created by the diffuse phase transitions. The temperature range will typically vary with the frequency used in the measurement. The breadth of the phase transition depends mostly on the amount of disorder in the structure. Largely disordered structures will have a wider peak than those with less disorder. Each compositional fluctuation in the material will exhibit its own peak dielectric constant. These individual units combine together to form a broad peak that is composed of many smaller compositional peaks. If each compositional unit had a peak  $K$  at different temperatures, the material peak would extend over the range of temperatures of the individual units. This broad peak can be thought of as a global average of the peaks created by the individual disordered units. The disordered material basically acts like a composite matrix where each section has an effect on the overall properties of the matrix.



## CHAPTER-3

### LITERATURE REVIEW

#### Primary difference between BNT and PZT based ceramics

- BNT is a ferroelectric compound with complex ion ( $\text{Bi}_{0.5}\text{Na}_{0.5}$ ) of  $\text{Bi}^{3+}$  and  $\text{Na}^{+}$  in the A-site.
- PZT is the solid solution which is composed of ferroelectric  $\text{PbTiO}_3$  and antiferroelectric  $\text{PbZrO}_3$ .
- BNT based ceramics which are made of ferroelectric BNT and other ferroelectrics or nonferroelectrics such as  $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ ,  $\text{BaTiO}_3$ .
- BNT- based ceramics are piezoelectric materials with the complex in their A-site, and the ceramics with relatively good piezoelectric properties can be obtained through partially substitution of A-site ( $\text{Bi}_{0.5}\text{Na}_{0.5}$ )<sup>2+</sup> ions by  $\text{Ba}^{2+}$ , ( $\text{Bi}_{0.5}\text{K}_{0.5}$ )<sup>2+</sup>, and so on.

#### **Problems with pure BNT System**

- Large coercive field ( $73\text{Kv/cm}^2$ )
- Difficult to poll
- Low piezoelectric property
- Surface often become conducting
- High Loss

#### Why BNT-BT ?

- Promising lead free ceramic

- Improved dielectric and piezoelectric properties at MPB
- Doping with rare earth metals made BNT conducting

### **Sol-gel combustion synthesis of BNBT powders**

- Synthesized by citrate nitrate sol gel combustion method with composition  
 $0.94[(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3]-0.06\text{BaTiO}_3$  (BNBT)
- Precursors taken are using barium acetate, bismuth nitrate, sodium nitrate and a peroxy-citrate complex of titanium isopropoxide as starting precursors.
- Powders are Calcined at temp  $500^{\circ}\text{C}$
- C/N ratio was taken to be 0.2
- Citric acid to metal cation ratio was 2.5:1
- Samples are sintered at  $1100^{\circ}, 1150^{\circ}\text{C}$  for 2 hrs
- $d_{33}$  for BNBT was found to be 125pc/N &  $K_p$  was found to be 0.272

### **Problems**

1. Urea was added in order to prevent precipitation in ratio with metal cation i.e. 1.4:1
2. The combustion powder shows high degree of agglomeration of particle so the powder was ball milled for 24 hrs
3. Densification problem

### **Synthesis, ferroelectric and piezoelectric properties of some**

#### **(Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub> system compositions:**

- Synthesized By Citrate method of composition  $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ ,  $(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ ,  $(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3+0.4\text{wt}\%$  of CoO.
- C/M ratio was controlled in the range 1.0-2.0. Best result were found where C/M =1.25
- Calcination temp. was taken to be  $500^{\circ}, 650^{\circ}\text{C}$  for 1hrs. Sample calcined at  $650^{\circ}\text{C}$  shows fine particles of 100-200nm.

- Sintering temperature was 1150<sup>0</sup> c for 2hr.
- XRD of NBT reveals the rhombohedral symmetry but in NBBT & NBBTC ceramics mix phase was found.

For pure NBT Pr in  $\mu / \text{cm}^2$  was 33.3 &  $E_c=80\text{Kv/cm}$

For NBBT Pr in  $\mu / \text{cm}^2$  was 37.1 &  $E_c=42.7\text{Kv/cm}$

For NBBTC Pr in  $\mu / \text{cm}^2$  was 25.6 &  $E_c=44.8\text{Kv/cm}$

- $d_{33}$  For pure NBT is 92pc/N

$d_{33}$  For NBBT is 180pc/N

$d_{33}$  For NBBTC is 58pc/N

- $K_p$  For pure NBT is 18.6

$K_p$  For NBBT is 27.6

$K_p$  For NBBTC is 25.8

## **PROBLEM**

Pure BNT prepared in this method has high coercive field 80 Kv/cm

Particles size are of 100-200nm.

### **Effects of Substitution in A- and B-site Cations of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$**

- Since the BNT composition has a high coercive field E, of 73 kV/cm it is thus difficult to achieve successful poling. This leads to low piezoelectric properties. To improve the dielectric and piezoelectric properties of BNT, *several* solid solutions of BNT with  $\text{PbTiO}_3$ ,  $\text{SrTiO}_3$  were studied. The last two solid solutions with proper compositions are suitable for piezoelectric actuator applications.

- Another way to improve the properties of BNT is by the addition of a modifier such as a rare-earth element. The addition of La to replace the Bi and Na sites was found to induce lattice distortion and cause changes *in* microstructure and dielectric and piezoelectric properties. It was also found that the dielectric anomaly and abnormal dielectric loss of BNT at high temperatures were *suppressed* with the La-substitution.
- Samples were prepared by a conventional mixed oxide method.
- Raw materials were  $\text{Bi}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Nd}_2\text{O}_3$  powders with purity of at least 99.5% (reagent grade).
- Calcination was carried out at  $900^\circ\text{C}$  for 2 hr.
- All specimens were sintered in a free control atmosphere at  $1150^\circ\text{C}$  for 2 hrs.
- The pellets were polled in a silicon oil bath at  $50^\circ\text{C}$  with a DC field of 50-70 kV/m for 5 minutes.
- However, no *sign of any* phase change was detected in all compositions which indicate that the rhombohedral ferroelectric structure of BNT provides flexibility for incorporating a small amount of these additives.
- *All* specimens were sintered at  $1150^\circ\text{C}$  for 2 hrs to obtain at least 95 % of their theoretical densities.

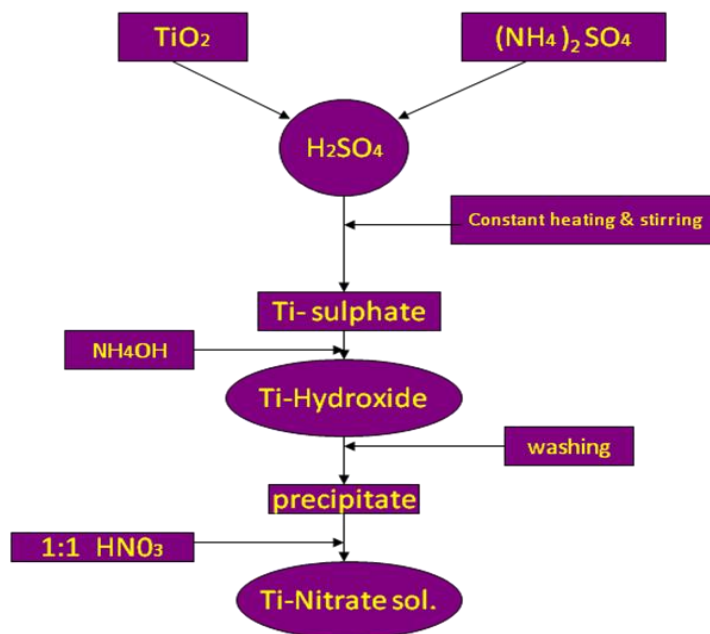
High purity  $\text{Bi}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{TiO}_2$ ,  $\text{BaCO}_3$  and  $\text{ZrO}_2$  (purity 99.0%) powders were used as starting materials. Our preliminary experiments found that BNT–BZT ceramics were not well synthesized by mixing and calcinating all these above powders as used in the conventional oxide mixing process. The BNT BZT ceramics were therefore prepared by using a modified two-step sintering approach, in which BNT and BZT source powders were calcined separately and then blended together. To prepare the BNT source powder,  $\text{Bi}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{TiO}_2$  powders were milled in alcohol using corundum balls for 4 h and dried at  $70^\circ\text{C}$  for 4–5 h, followed by calcining at  $850^\circ\text{C}$  for 3 h in air.  $\text{Ba}(\text{Ti}_{0.942}\text{Zr}_{0.058})\text{O}_3$  powder, the composition of which was reported to be near the MPB of BZT system [14,15], was also prepared from the corresponding starting chemicals under the same condition, except a higher calcination temperature of  $1200^\circ\text{C}$ . The BNT and BZT source powders were then weighted and blended according to the formulas of  $(1-x)\text{BNT}-x\text{BZT}$  (abbreviated to BNT–BZT100x), where x is the fraction of BZT, ranging from 0 to 12 mol%. After ball-milling in alcohol for 2

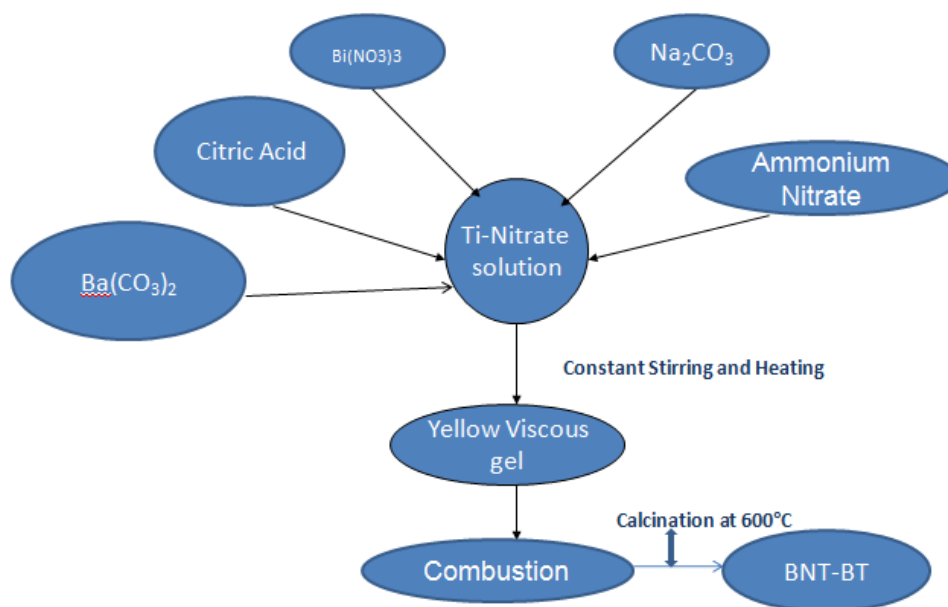
h and drying, the blended powder was die-pressed into discs of 10 mm in diameter and 1–2 mm in thickness. The small disc samples were sintered at 1180 °C for 3 h in air. The two circle surfaces of the sintered ceramic discs were polished and coated with silver paste as the electrode. To measure relevant electric properties, the prepared ceramic samples were polarized in silicone oil at 60 °C under 4.0 kV/mm for 30 min.

### **Powder synthesis**

BaTiO<sub>3</sub> powder was prepared following the solid-state synthesis by firing at high temperature a mixture of BaCO<sub>3</sub> (Merck, 99%) and TiO<sub>2</sub> (Merck, 99%). The processing steps were: ball milling for 2 h, calcining at 1150 °C for 4 h then mixing the calcined product for 3 h. The second way to make BaTiO<sub>3</sub> powder was a coprecipitation process and Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> was dissolved in an aqueous solution of oxalic acid. Titanium hydroxide precipitated and reacted with oxalic acid to form soluble TiOC<sub>2</sub>O<sub>4</sub>. When the solubilisation of titanium was complete, barium acetate was added slowly and a double oxalate BaTiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O was obtained. The processing steps of the coprecipitation process may be described by these equations: The calcination of the precursor powder is made at 650 °C for 10 h and an additional treatment is made at 800 °C for 4 h in order to control the grain growth.

The thermal behaviour was studied by DTA–TG under flowing air (TG96, Setaram). Approximately 50 mg of the precursor mixture was accurately weighed in an alumina crucible. The temperature was raised from room temperature to 1200 °C at 10 °C/min under air flow. Grains size distribution was controlled by a laser Coulter LS130 granulometer and a specific area analyser Monosorb Quantachrom (based on BET theory)

**EXPERIMENTAL DETAILS:**Ti-Oxynitrate solution**Preparation of (1-x)BNT-XBT**



## PREPARATION OF BNT (0.94)- BT(0.06).

### 1. COMBUSTION METHOD

Ti solution=50ml.

$$50 \text{ ml of Ti solution} = 0.1718/20 = 8.59 \times 10^{-3}$$

$$\text{Moles of Ti in BaTiO}_3 = 8.59 \times 10^{-3} \times 0.06 = 0.5154 \times 10^{-3}$$

$$\text{So moles of Ba} = 0.5154 \times 10^{-3}$$

$$\text{Weight of BaCO}_3 = 0.514 \times 10^{-3} \times 197.35 = 101.71 \times 10^{-3} \text{ gm}$$

$$\text{Moles of Bi} = 8.59 \times 10^{-3} \times 0.94 \times 0.5 = 4.0373 \times 10^{-3}$$

$$\text{Weight of Bi(NO}_3)_3 = 485.07 \times 4.0373 \times 10^{-3} = 1958.373 \times 10^{-3} \text{ gm}$$

$$\text{Moles of Na}_2\text{CO}_3 = 8.59 \times 10^{-3} \times 0.94 \times 0.5 \times 0.5 = 2.01865 \times 10^{-3}$$

$$\text{Weight of Na}_2\text{CO}_3 = 2.01865 \times 10^{-3} \times 105.99 = 213.9567$$

Specific gravity of HNO<sub>3</sub>=1.42

Molecular weight=63.01

Percentage pure=69.5

1275ml of Ti solution contains =500ml of HNO<sub>3</sub>

100ml of Ti solution contains=39.21ml

Mass of nitrate=vol\*specific gravity\*percentage pure

$$=1.42*34.21*69.5$$

$$=38.69\text{gm}$$

Number of moles of  $\text{NO}_3 = \text{mass}/\text{M.W of HNO}_3 = 38.69/63.01 = 0.614\text{mole}$

Fuel:Oxidising agent=0.1

Citric acid =  $0.1*0.614 = 0.0614\text{mole}$

Amount of citric acid =  $0.0614*192.13 = 11.79\text{gm}$

For 50ml of Ti solution citric acid used =  $11.79/2 = 5.895\text{gm}$

Total moles of metal =  $(0.1718/20)*2 = 0.01718$

Moles of  $\text{NH}_4\text{NO}_3 = 0.0178*6 = 0.10308$

Weight of  $\text{NH}_4\text{NO}_3 = 0.10308*80.04 = 8.2505\text{gm}$

For 50ml of Ti solution  $\text{NH}_4\text{NO}_3$  used =  $8.2505/2 = 4.1252\text{gm}$

M: $\text{NH}_4\text{NO}_3 = 1:3$

M:Citric acid=0.2

## Details

50 ml of Ti solution

$\text{Bi}(\text{NO}_3)_3 = 1.9583\text{gm}$

$\text{Na}_2\text{CO}_3 = 0.2139\text{gm}$

$\text{BaCO}_3 = 0.10171\text{gm}$

$\text{NH}_4\text{NO}_3 = 8.2505\text{gm}$

Citric acid =  $5.895\text{gm}$



## **CHAPTER-5**

### **RESULTS AND DISCUSSIONS**

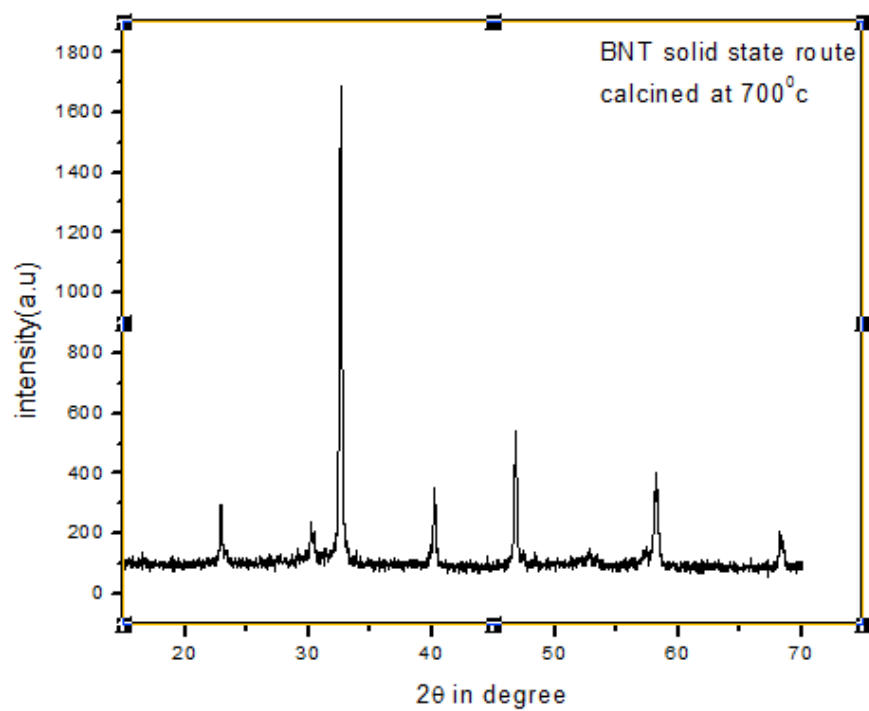


Fig.1 XRD of BNT calcined at 700°C by solid state route

Fig.1 shows that BNT prepared by solid state route contains small amount of impurity.

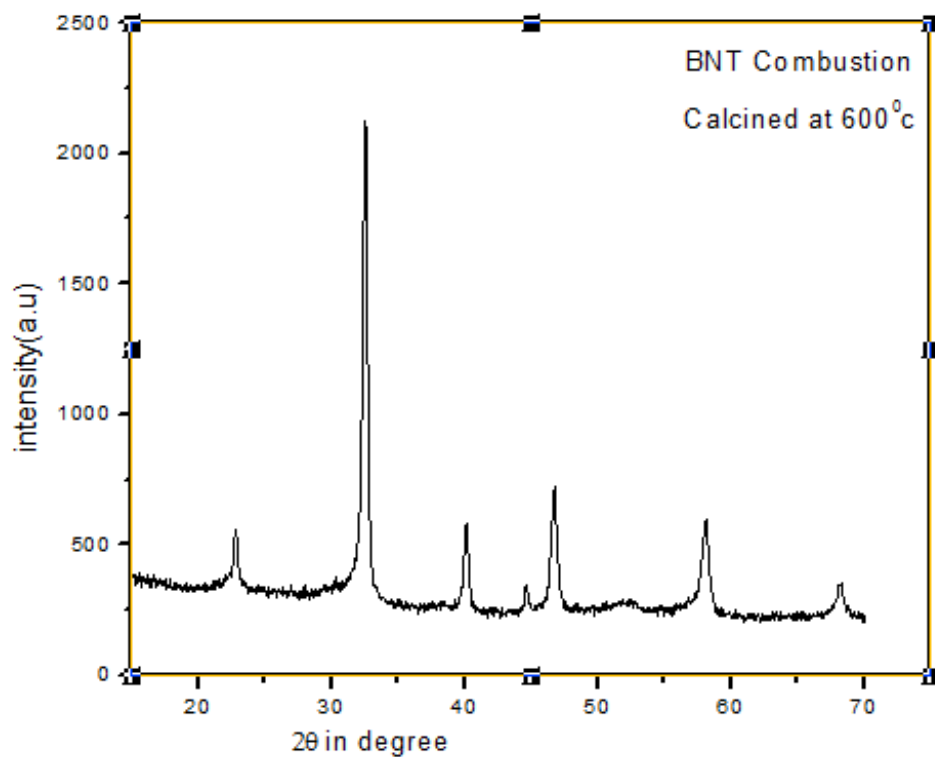


Fig.2 XRD of BNT calcined at 600°C by combustion process

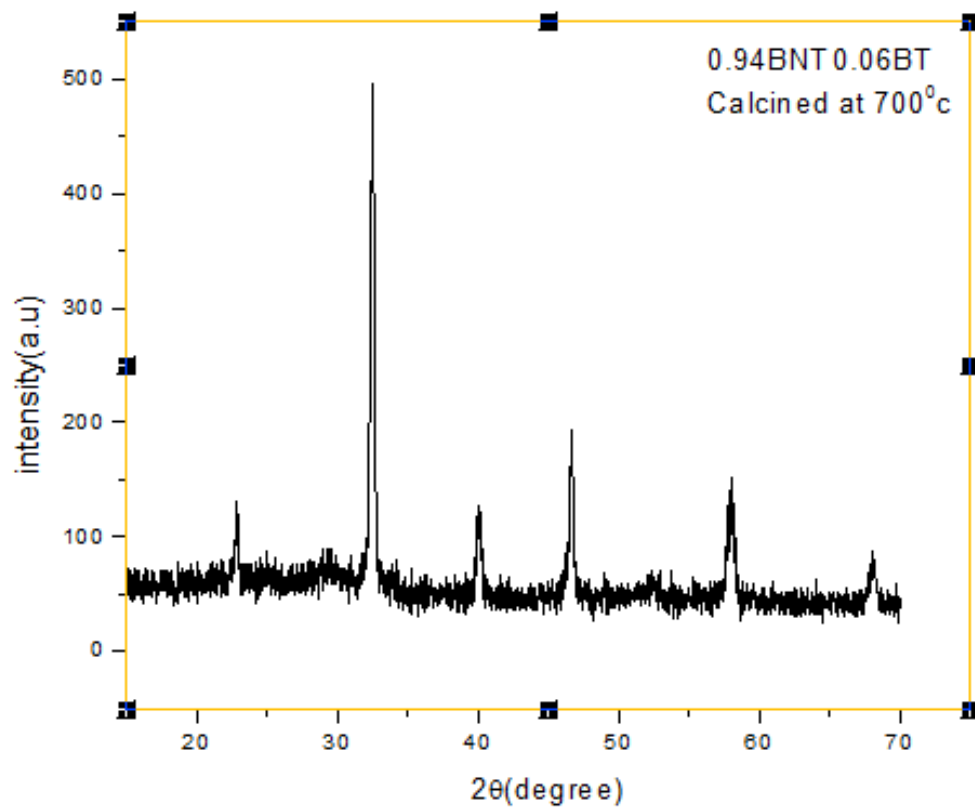


Fig.3 XRD of 0.94 BNT 0.06BT calcined at 700°C by solid state route

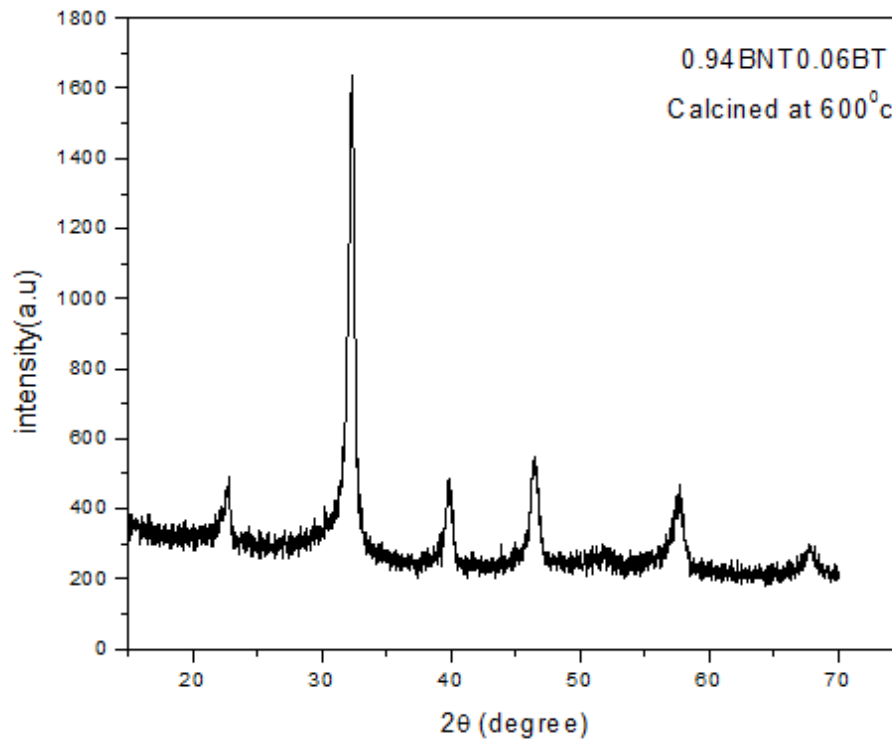


Fig.4 XRD of 0.94 BNT 0.06 BT calcined at 600°C by combustion process

Fig.2 shows that phase pure BNT can be prepared at 600°C by combustion synthesis method. 0.94BNT-0.06BT also can be synthesized at 600°C. In case of solid state method impurity phase reduced with BT addition. Now powders were taken for sintering and further characterization.

DRY WEIGHT.

BNT	BNT(0.94)-BT(0.06)
0.6338gm	0.6719gm
	0.6632gm

SUSPENDED WEIGHT

BNT	BNT(0.94)-BT(0.06)
0.5515gm	0.5783gm
	0.5738gm

SOAKED WEIGHT

BNT	BNT(0.94)-BT(0.06)
0.6606gm	0.6805gm
	0.6730gm

Density of BNT = [Dry weight/(soaked weight-Suspended weight)]\*0.81

DENSITY

BNT	BNT(0.94)-BT(0.06)
4.705gm/cc	5.325gm/cc
	5.415gm/cc

Average density of BNT(0.94)-BT(0.06)=5.37gm/cc. Theoretical density is 5.9gm/cc, So density percentage=91.01

**Conclusion:**

Phase pure BNT- BT powder can be prepared at a temperature as low as 600°C by auto-combustion route. It is very difficult to prepare phase pure solid solution system by conventional solid state synthesis method. 96% of theoretical density was achieved for combustion synthesized powder. For Solid state synthesised powder it is difficult to achieve more than 92% of theoretical density.

## CHAPTER-6

### FUTURE WORK

- To achieve lower polling field for polling BNT
- Study of dielectric behavior with temperature
- P-E hysteresis loop
- Polling
- Particle size analysis of calcined powder

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