

**Synthesis and characterization of $\text{Na}_{0.5}\text{Bi}_{0.44}\text{Ba}_{0.06}\text{TiO}_3$ and
 $\text{Na}_{0.5}\text{Bi}_{0.44}\text{Ca}_{0.06}\text{TiO}_3$ ceramics system**

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In partial Fulfillment for the award of the degree of
MASTER OF SCIENCE
IN
PHYSICS

Under supervision of

Assistant professor Dr. Saket Asthana



DEPARTMENT OF PHYSICS
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2014-2016

APPROVAL SHEET

This Thesis entitled " synthesis and characterization of $\text{Na}_{0.5}\text{Bi}_{0.44}\text{Ba}_{0.06}\text{TiO}_3$ and $\text{Na}_{0.5}\text{Bi}_{0.44}\text{Ca}_{0.06}\text{TiO}_3$ ceramics system" is approved for receiving the degree of master of science in physics , Indian institute of technology, Hyderabad.

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CERTIFICATE

This is certify that thesis entitled " **synthesis and characterization of $\text{Na}_{0.5}\text{Bi}_{0.44}\text{Ba}_{0.06}\text{TiO}_3$ and $\text{Na}_{0.5}\text{Bi}_{0.44}\text{Ca}_{0.06}\text{TiO}_3$ ceramics system**" has been submitted by Soubhik kayal for receiving the degree of master of science in physics , Indian institute of technology, Hyderabad is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge , the matter incorporate in this project has not been capitulated yet to any other institution for the award of any degree in M.Sc physics.

Place:-Hyderabad

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ACKNOWLEDGEMENT

First of all I express my appreciativeness to Dr. saket Asthana for his all over support in every problem , valuable rendered to me and his acceptance of me as a M.Sc student working under his guidance. I am especially thankful to the phd scholar Mr. kumar raja kandula for his valuable suggestions and clarify all my doubts and helping me in completing my project and analyzing the data.

I also thankful to my M.Sc chemistry friend for clarifying some doubt related to the project especially Shakil Ahmed and also Abdul shiraj, Sourabh ghosh(phd scholar).

lastly but not the least I would like to express my gratefulness to my mother for her endless support at any circumstances without which I could not able to completed my project work.

Date:- 25.04.2016

Soubhik Kayal
SOUBHIK KAYAL

**THE WORK
IS
DEDICATED
TO
MY MAA**

ABSTRACT

Piezoelectric material finds its application in multiple devices such as sensors, actuators, printer etc. However most of the piezoelectric materials utilize lead based system which is having serious environmental issue. Currently there is no problem important than to find the replacement for the lead-based piezoelectric for the actuators. We need to develop electromechanical properties for the actuator application with high piezoelectric constant, high coupling constant, low loss, high transition temperature. So to solve the issue we have to focus on few things- i) search a new system that shows *Morphotropic (M)* or *Poly-morphotropic (P)* phase boundary, because at that boundary there is a thermodynamical phase transition due to that there should be a sharp peak for the piezoelectric constant also for stress that can give rise of high piezoelectric constant, dielectric constant ii) Stabilization of the metastable phase iii) Improve the intrinsic properties of the known composition through microstructure optimization, domain and cation engineering, multi layering. All those approaches are challenging to synthesize a material which has satisfied above those properties. As we going to execute those special properties in our known piezoelectric system which is having high *depolarizing temperature* shows huge impression in the piezoelectric based research.

In the first chapter we study the NBT-BT with 6% composition of the Barium into the Sodium Bismuth Titanate (NBT) to develop the *morphotropical phase boundary* (MPB) to improve electromechanical properties. Lead free $\text{Na}_{0.5}\text{Bi}_{0.5-x}\text{Ba}_x\text{TiO}_3$ and $\text{Na}_{0.5}\text{Bi}_{0.5-x}\text{Ca}_x\text{TiO}_3$ ceramics has been prepared by solid state reaction process with composition of $x=0.06$. From XRD pattern it is confirmed that the NBT-BT (6%) and NBT-CT (6%) single phase were formed. The RAMAN pattern shows roughness or irregularity due to the data taken at resolution. From morphological study by SEM it is found that the grains were well developed and have dense structure. Also the grain shape /size have changes from granular to plated shape at different sintering temperature. We also study the impedance analyzing and it is found that both real and imaginary impedance decreases with increasing of the frequency and the temperature. May be due to the rising of the temperature there should be the release of space charge that leads to reduction of the barrier properties that may be a responsible factor for the enhancement of the ac

conductivity , hence we Know conductivity is inversely proportional to the impedance that gives decreasing of the impedance with temperature. We also study dielectric measurement to study the dielectric behavior with respect to different temperature. In the second chapter we study the NBT-CT with 6% composition of the calcium into the Sodium Bismuth Titanate (NBT) to develop the morphotropical phase boundary to improve the electromechanical properties.

In the lead based piezoelectric material with B-site disorder the origin of the enhancement of the piezoelectric properties near the morphotropical phase boundary has been associated with the present of the intermediate monoclinic/orthorhombic phase. However in lead free NBT-BT (6%) and NBT-CT with A-site disorder has not been conclusively established. They shows morphotropical phase boundary with the present of the intermediate *Rhombohedral/Tetragonal* phase and *Rhombohedral/Orthorhombic* phase respectively.

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CHAPTER-1

➤ INTRODUCTION:-

Dielectric is basically electric insulator. In such materials electrons are tightly bound to the atoms thus they couldn't conduct any electrical current. In dielectric center of the positive and the negative charged ion's center of mass coincides at a point. So there is lack of dipole moment so no conductivity is possible. A sufficient amount of electric field when applied to a crystal then the center of positively charges slightly displaced in the direction of the field and the negative charge in the opposite direction. This produces electric dipoles throughout the crystal. And the crystal is said to be polarized.

Examples of the dielectric are: glass, porcelain, pure water, wood, etc.

1.1. POLARIZATION:-

When a dielectric material is placed to an external electric field, then it becomes polarized in a small volume of substance then the geometric sum of the electric dipole moment vectors of the molecules becomes nonzero.

The polarization 'P' is defined as the sum of the electrical dipole moment per unit volume.

$$\mathbf{P} = \Sigma \mathbf{p} / \mathbf{v}$$

If the number of molecules per unit volume is 'N' and each dipole has a moment 'p' then the polarization is given by,

$$\mathbf{P} = N\mathbf{p}$$

1.2. FREQUENCY DEPENDENCY OF POLARIZATION:-

Electric polarizability of any atom is interpreted as dipole moment per local electric field

$$\alpha = p / E_{loc}$$

The net *polarizability* (α) of a dielectric material results mainly from four contributions and those are given below:-

i) Space charge polarizability:-

Due to the space charge current their arises space charge inside the electrode where positive and the negative charge are displaced by some amount as a result there appears polarization that produce the *Space charge polarizability*.

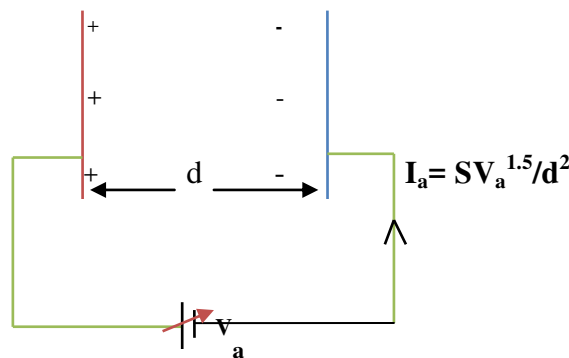


Fig.1. - Schematic diagram for space charge formation

ii) Dipole polarizability:-

A molecule such as H₂O, having a permanent dipole moment is called a dipole or polar molecule and a substance comprising such molecule is called a dipole substance. The dipolar polarizability is the property of the dipole substances. In the absence of an external electric field, the dipole has random orientations and therefore no net polarization. However, when we apply the electric field then the dipole orient themselves along the field and produce *Orientalional polarizability* or *Dipolar polarizability*.

The equation for the Dipolar polarizability is-

$$\alpha_d = (\text{dipole moment}) / (\text{electric field}) = p^2 / 3KT$$

Where,

p=Dipole moment

T=Temperature

At the room temperature, $\alpha_d \sim 10^{-39} \text{ fm}^2$

c) IONIC POLARIZABILITY:-

The ionic polarizability arises due to displacement of a charged ion relative to other ions in a solid. assuming the forces near equilibrium as simple harmonic, the displacement " Δx " in the presence of an electric field 'E' is given by,

$$\beta \Delta x = eE$$

Where, ' β ' is the force constant. Thus the ionic polarizability is determined as

$$\alpha_i = (\text{dipole moment}) / (\text{electric field}) = p/E = (e \Delta x) / E = e^2 / \beta$$

For $\beta \sim 20 \text{ Nm}^{-1}$, $\alpha_i \sim 10^{-39} \text{ fm}^2$, ionic contribution is important in the low frequencies.

d) ELECTRONIC POLARIZABILITY:-

Electronic polarizability appears due to dislodge of the electron cloud of an atom with respect to its nucleus in the presence of an applied field. The polarization as well as the dielectric constant of a material is at optical frequency results mainly from the *Electronic polarizability*. At the optical frequencies the by depending upon the quantum theory we achieved the polarizability equation for the electronic polarizability-

$$\alpha_e = (e^2/m) \sum_j f_{ij} / (\omega_{ij}^2 - \omega^2)$$

Where

f_{ij} known as the oscillator strength of the electric dipole transition between the atomic states i and j .

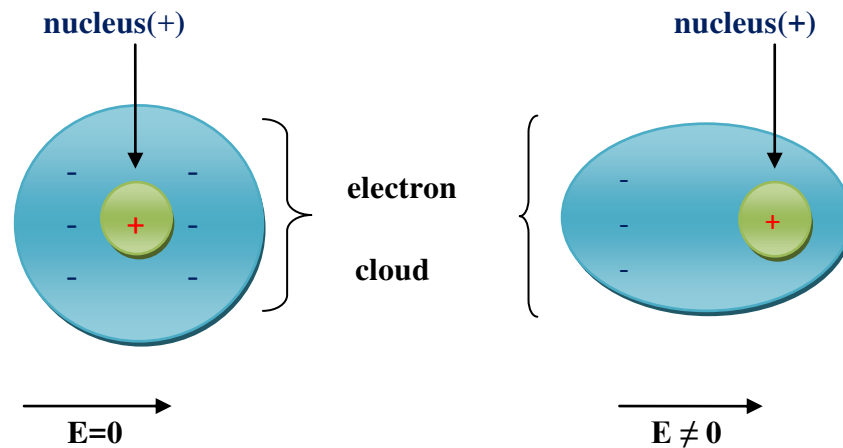


Fig.2. - Schematic diagram for understanding the electronic polarization in the presence of the external electric field

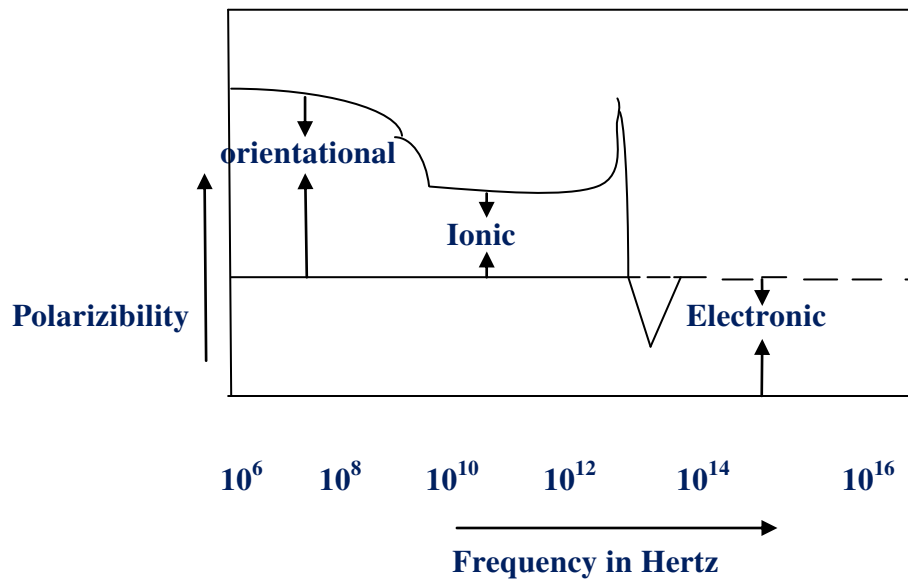


Fig.3:- schematic diagram of polarizability versus frequency

1.3. CLASSIFICATION OF SYMMETRY CLASSES (POINT GROUP):-

There are 32 symmetry classes or point group out of which 21 point groups are noncentrosymmetric or having lack of inversion symmetry. Here we are all interested in these 21 point groups those are special because they posses dipoles. Again out of the 21 point group, 20 show piezoelectric behavior. Out of those 20 point groups, 10 point groups have unique polar axis (polarizes with the application of the electric field) are exhibiting pyroelectric effect. These 10 divided into ferroelectric and non-ferroelectrics.

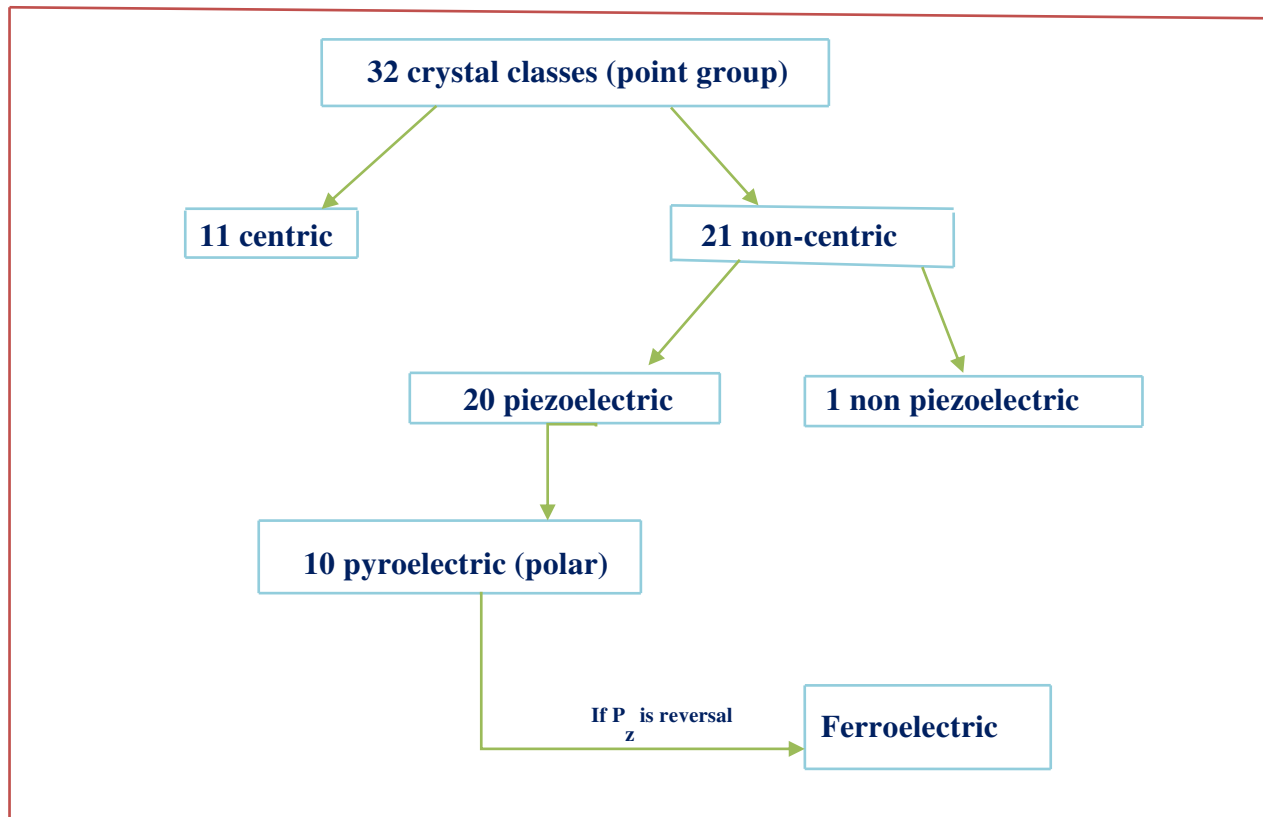


Fig.4. - A classification scheme for the 32 crystallographic (in 3D) point groups

1.4. FERROELECTRICITY:-

Ferroelectricity is a property which refers to the state of spontaneous polarization, i.e., polarization of the material at the absence of the electric field. The crystal displayed ferroelectricity is called ferroelectric crystals. In such crystals centers of the positive and the negative charges do not coincide with each other even in the absence of the electric field that leads to give the non-zero value of the *dipole moment*. Variation of polarization with respect to the electric field is not linear for such crystals but forms a closed loop called the hysteresis loop. The ferroelectricity vanishes above a certain temperature called the Curie temperature. The spontaneous polarization (P_s) in ferroelectric can be reoriented into two or more equilibrium state under application of the electric field. Ferroelectric material posses crystallographic allowed directions of spontaneous polarization called the polar axis. Moreover this region having uniform polarization inside the ferroelectric called the ferroelectric domain. These domains are formed to minimize the electrostatic energy of depolarizing field and elastic energy associated to the mechanical strain produced upon cooling through phase transition. Interface between two domains called the domain wall.

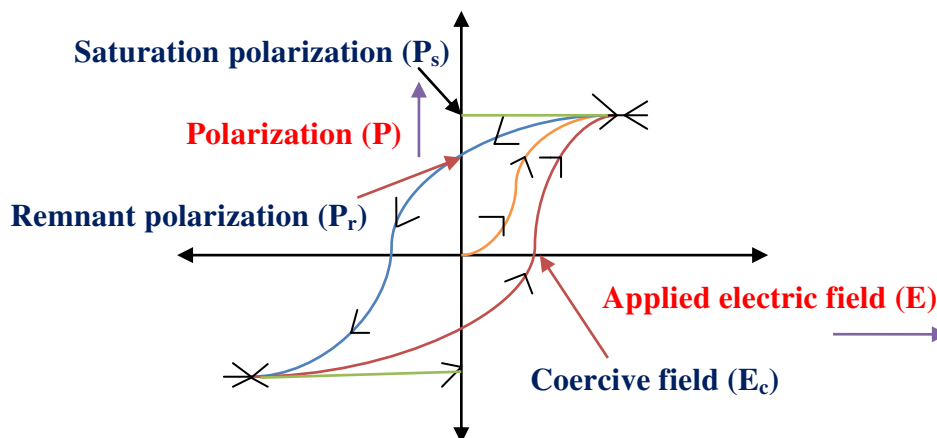


Fig.5. - A typical polarization (P) - applied electric field (E) hysteresis loop for ferroelectric material

This is mainly field induced polarization, because the field is not large enough to cause orientation of the ferroelectric domain. With further increasing the electric field the polarization increases non-linearly with the applied field, because all the domains start to orient along the domain. At the high field polarization will reach a state of saturation where most domain are aligned along the applied electric field to achieve a mono domain state to get the low energy state because polarization energy(E) = - (polarization direction)*(applied electric field direction). The extrapolation of the linear segment of the curve at high field to the polarization axis called the spontaneous polarization (P_s). When the external field reversed then all the domain can not to the original state due to pinning of the domain wall that give rise to the remnant polarization(P_r) at zero electric field. Remnant polarization can be removed further by applying electric field in opposite direction and the critical field is required for this is called **coercive** field (E_c). On further increasing of the electric field along negative direction and the cycle can be completed by switching the field direction again.

Order parameter of the system defines the orderings of the system which are having some definite value in one phase and having zero value in the other phase changing of the order parameter gives the phase transition. In the ferroelectric system order parameter is the spontaneous polarization so for changing the value of the spontaneous polarization from non zero value to zero that definite give raise to the phase transition .There are two type of phase transition can be possible (with the increase of the temperature the spontaneous polarization deceases for atypical ferroelectric material) - i) If polarization suddenly drops to zero at a critical temperature then this phase transition can be called as the first order phase transition. ii) On the other case if the polarization decrease continuously with increasing of the temperature then this phase transition is called second order phase transition. When the system cool down to the Curie temperature again order parameter changes and via structural changes of the system loses its center of symmetry and becomes to its ferroelectric state.

Some time high dielectric permittivity at T_c (*Curie temperature*) shifted towards the room temperature by doping to get the high relative permittivity at the room temperature. The shifting

of T_c towards RT give leads to an enhanced piezoelectric response suggesting the important role played by structural instability. The structural instability has been considered an important factor in enhance piezoelectric response in solid state solution near morphotopical phase boundary (*MPB*). In this thesis, we therefore investigate the effect of the structural instability on piezoelectric response respect to the lead free Sodium Bismuth Titanate (NBT) solid solution like- NBT-BT (6%) and NBT-CT (6%).

The ferroelectric crystals can be classified into the two main groups-

i) Order- Disorder group:-

In the order disorder class of ferroelectric transition is associated with individual ordering of the ions. In some crystal which contain hydrogen bonds in which the motion of the protons leads to produce *ferroelectricity*.

Examples; Potassium Dihydrogen Phosphate (KH_2PO_4), Rubidium Hydrogen Phosphate (RbH_2PO_4), etc.

ii) Displacive group:-

Displacive group of ferroelectrics is the one in which the ferroelectric transition is incorporated with the displacement of a whole sub-lattice of one type relative to a sub-lattice of another type. The crystals of this class having structures which are closely related to the *Perovskite* and *Ilmenite* structure (in our purpose we are using the perovskite material).

Examples: BaTiO_3 , KNbO_3 , LiTiO_3 , $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT).

➤ **Mechanism:-**

In our purpose we use NBT as a host material in that material Na^+ and Bi^{3+} are alternatively occupying at the corners of the cubic unit cell, O^{2-} ions occupying the face center Ti^{3+} ion occupying the body center of the cube. Thus each Ti^{3+} ions are surrounded by six O^{2-} ions in an octahedral configuration.

However, for $T < T_c$ the Ti^{3+} and Na^+ and Bi^{3+} ions slightly moves upward while the O^{2-} ions slightly move downward. Thus the positive and negative charges do not coincide with other. This produces the spontaneous polarization in the crystal.

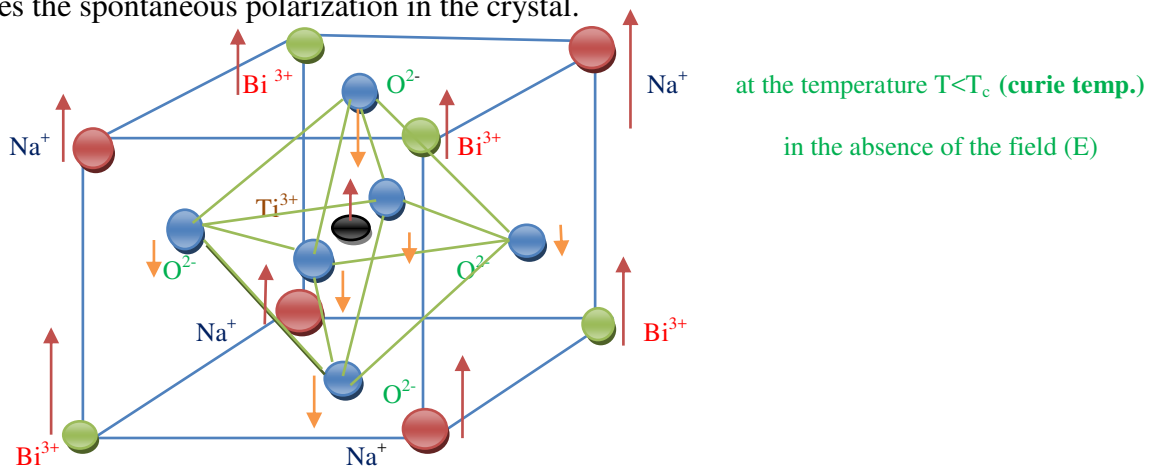


Fig.6. - Sodium Bismuth Titanate (NBT) crystal structure

1.5. PIEZOELECTRICS:-

In some crystal, the application of an external stress induces a net dipole moment which produces the electrical polarization with the polarization charges appearing on the surface of the crystals. Such crystals are called piezoelectric crystals and the phenomenon is known as the *piezoelectricity*.

A material either be piezoelectric, pyroelectric or ferroelectric only if its crystal symmetry is inherently asymmetric, i.e., it lacks an inversion center or having *non centrosymmetric* structure. In the 32 crystal symmetry classes only eleven exhibit center of symmetry, in another one case a combination of symmetries effectively provides such a center, leaving twenty classes which have asymmetric properties. All the crystals in these twenty classes are piezoelectric. When such a noncentrosymmetric crystal is subjected to a mechanical stress the ions are

Displaced from each in an asymmetric manner and the crystal become electrically polarized. This is called *piezoelectric effect*.

The piezoelectric effect has usually used to convert electrical energy into mechanical energy, and also vice-versa. The existence of direct of direct effect and its inverse is to be distinguished from a similar property called *electrostriction*.

The piezoelectric equations are:-

$$\mathbf{P} = \mathbf{Z} \mathbf{d} + \epsilon_0 \mathbf{E} \chi \text{i)}$$

$$\mathbf{e} = \mathbf{Z} \mathbf{s} + \mathbf{E} \mathbf{d} \text{ii)}$$

where "P" representing the polarization , "Z" defines stress , "d" is the piezoelectric strain constant, "E" the electric field , " χ " representing dielectric susceptibility , "e" the elastic strain and s the electric compliance constant. First equation exhibits the development of polarization by an applied stress and the second one shows the development of elastic strain by an applied electric field.

Another important parameter for characterization of the piezoelectric material is the electromechanical coupling constant, which depicts the ability of the material to convert one kind of energy to other. The general form of the coupling constant is defined by -

$$\mathbf{K} = \sqrt{(\text{stored electrical energy}) / (\text{supplied mechanical energy})} \text{ii)}$$

Or,

$$\mathbf{K} = \sqrt{(\text{stored mechanical energy}) / (\text{supplied electrical energy})} \text{ii)}$$

Value of "K" is always less than one due to incomplete conversion of energy because from second law of thermodynamics tells us complete conversion of energy is not possible or the energy efficiency is always less than unity.

Some examples of such crystals are Quartz, Rochelle salt and Tourmaline. Generally, piezoelectric material having high values of the "d" coefficient and "K" are desired for the actuator application.

1.6. PYROELECTRICITY:-

Pyroelectricity is the ability of certain material to generate a temporary voltage when they are heated or cooled. The change in the temperature modifies the position of the atoms slightly within the crystal structure as a result polarization of the system got changed. This polarization gives rise to a voltage across the crystal. If the temperature stays constant at its new value, the pyroelectric voltage disappears due to the leakage current.

It is mentioned earlier that 10 out of 21 non-centrosymmetric classes of material show spontaneous polarization which response the temperature is called pyroelectric effect.

$$\Delta P = \lambda \Delta T$$

Where,

ΔP = Spontaneous polarization

λ = Pyroelectric polarization

ΔT = Change in temperature

Increasing in temperature leads to decrease in spontaneous polarization. Polarization suddenly falls to zero on heating above particular temperature. These results do thermal agitation with increase in temperature, leading to opposition of the dipoles to align in particular direction.

1.7. INTRODUCTION TO THE LEAD FREE PIEZOELECTRIC:-

Lead based piezoelectric material with perovskite structure based on *lead zirconate* (PZT) are widely used for actuators, MEMS, sensors etc because of their excellent piezoelectric properties. In the lead based piezoelectric material with B-site disorder the origin of the enhancement of the piezoelectric near the morphotropical phase boundary has been associated with the present of the intermediate *Monoclinic/ Orthorhombic* phase. However due to the high toxicity of lead based ceramics has caused serious environmental pollution issue. Therefore, it is necessary to introduce new lead free piezoelectric material with comparing ferroelectric properties with PZT for replacing them.

After wide range of research in 1961 *Sodium Bismuth Titanate* (NBT) was discovered by *Smolenskii*. It is widely used ferroelectric material because of it has high temperature dielectric constant. Sodium bismuth Titanate (NBT) is an ABO_3 distorted perovskite which exhibit *Rhombohedral* crystal structure at room temperature. It has been reported NBT is a relaxor ferroelectric having diffuse phase transition from *Rhombohedral to Tetragonal* phase 200°C to 320°C and from *Tetragonal to Cubic* phase 540°C . NBT structure has shown in Fig.7. Where bismuth and sodium cations occupy the corner positions of a cubic unit cell, oxygen cations occupy the face center positions, and one titanium cations in the center of the oxygen produce *octahedral* phase.

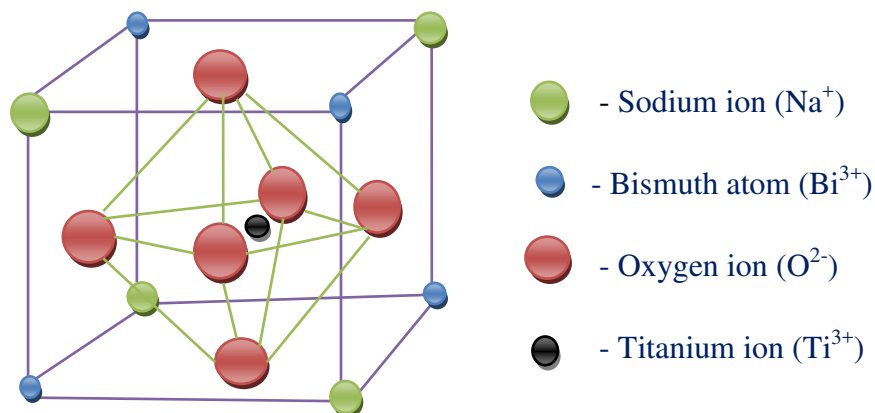


Fig.7. - Structural representation of the Sodium Bismuth Titanate (NBT)

CHAPTER 2

➤ **MOTIVATION:-**

- i) In previous days Lead based material have used as piezoelectric material due to existence of the morphotropical phase boundary(MPB) Monoclinic/Orthorhombic, but those had been widely studied for few decade, so need to develop a new material which show high ferroelectric property compare to that of the Lead based material.
- ii) *Perovskite* material having wide range application in various fields like sensors, motors (actuators), pyroelectric devices, printer and many more.
- iii) Electrical properties can also be enhanced by proper lanthanide doping or by producing the solid state solution.
- iv) Leakage current issue that decreases the ferroelectric properties can be modifying by the cation engineering (proper lanthanide material doping).
- v) In few applications we need high spontaneous polarization (P_s) and low coercive field (H_c) basically in ferroelectric memory device application like *Fe-RAM* (ferroelectric random access memory). Softness of the ferroelectric material can be increased by decreasing of its anisotropy by preparing the solid state solution.

➤ **THESIS OBJECTIVE:-**

- i) At high temperature Lead get evaporate from the Lead based material and also lead is not good for both health and environment, so need to develop a new harmless material for replacing the lead based piezoelectric.
- ii) To prepare solid state solution of Sodium Bismuth Titanate (NBT) , NBT-BT with 6% composition of Barium Titanate ($\text{Na}_{0.5}\text{Bi}_{0.44}\text{Ba}_{0.06}\text{TiO}_3$) and NBT-CT with 6% composition of Calcium Titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ca}_{0.06}\text{TiO}_3$).

iii) To study the effect of NBT due to addition of 6% composition of Barium Titanate (BT) and Calcium Titanate with NBT whiskers by performing different structural, morphological and electrical characterization.

2.1. LITERATURE REVIEW:-

Lead free Sodium Bismuth Titanate (NBT) was discovered by *Smolenskii* et al. in 1960. The existence of the *Rhombohedral* symmetry was found out by Jones and Thomas in 2002. When, heated then its structural transition takes place from *Rhombohedral* to the *Cubic*. This NBT material having high Curie temperature can be used in high temperature application. In NBT there are many issues like *high coercive field*, *leakage current*, *dielectric loss* when high electric field have used. Different dopants (**Ba, Pb, Sr, Zr, La, K, and Bi**) can be added to NBT to combat some of its drawbacks, such as to decrease the coercive field and increase piezoelectric constant.

C.C. Wang et all investigate (1-X) NBT-X BT where one of the most advantage is the formation of the morphotropical phase boundary(MPB) at $0.5 < X < 0.8$ between *Rhombohedral* and the *Tetragonal* phase of the structure. Dielectric material near at *MPB* is interesting because they show anomalously large dielectric constant values compared to any other different composition. Since the phase transition is the first order (First order derivative of the Gibb's free energy is discontinuous) so at this point it shows anomalous ferroelectric properties.

XRD data depict variation of (200) and (111) peaks of NBT-BT samples with various BaTiO₃ content at RT. With the increasing of BaTiO₃ amount the shape of (200) *Rhombohedral* peak becomes asymmetric and finally get split in to (002) and (200) tetragonal peaks along with the *Rhombohedral* (200) peaks. But at concentration peak get merged with *Rhombohedral* (200) peak. They shown in this paper at the low concentration of the BT it stay in the *Rhombohedral* $X < 0.5$ but in the $X > 0.5$ structure transform to *Rhombohedral* to the *Tetragonal*.

P-E loop analysis give the maximum value of the *spontaneous polarization*, and *remnant polarization*, *coercive field* having the value $32.8 \mu\text{C}/\text{cm}^2$, $28.5 \mu\text{C}/\text{cm}^2$, $2.28 \text{ kv}/\text{mm}$. P-E become slimmer with increasing with the concentration of the BT further at $x=0.02$ remnant polarization and coercive field having value $6.7 \mu\text{C}/\text{cm}^2$ and $1.06 \text{ kv}/\text{mm}$ respectively, with increasing of the concentration decreasing value of the coercive field that confirms the anisotropy of the system gradually decreases that is why there is *negative strain* value at the zero field.

In the dielectric measurement they study the dependence of the dielectric constant, dielectric losses, dielectric impedance, dielectric electrical modulus with temperature and frequency from 20° - 400° C and 100 Hz to 100 kHz respectively. With the increasing of the frequency permittivity decreases at 1 KHz Maximum Permittivity decreases from the value ~ 6170 to 5000 . There are two characterization temperature T_d and T_m at the former temperature dielectric loss getting maximum value while permittivity is minimum and at latter one the opposite phenomenon is happening while loss getting minimum then permittivity getting maximum. In impedance measurement real and imaginary both impedances decreases with increasing of the frequency and the temperature and shows semiconductor behavior due to release of the space charge as a result of reduction in barrier properties in the material with rising temperature.

In Shodhganga paper they study FTIR spectrum of NBT-BT ceramics at room temperature in the range of 400 cm^{-1} to 4000 cm^{-1} . The bands at 658 cm^{-1} and 847 cm^{-1} are corresponds to the bending vibration of the Bi-O unit in $[\text{BiO}_3]$ and $[\text{BiO}_6]$ polyhedral units respectively and this vibration due to inter-polyhedral vibration. The presence of bands at the 1423 cm^{-1} and 1628 cm^{-1} are due to stretching vibration of BO_6 and TiO_6 in perovskite structure and this asymmetry stretching vibration goes to change the bond length of Ti-O bond along the c-axis and confirms the presence of oxygen group.

They investigate Raman spectroscopy for NBT-BT ceramics they observe de-convoluted Raman spectrum this is performed on the basis of 4 Gaussian-Lorentz modes. The existence of the Broad band in the spectrum are due to the creation of disorder in the lattice structure by the A-site ion and due to the overlapping of Raman modes. The atomic mass of the Ba^{2+} is in between the Na^{+} and Bi^{3+} ions and the ionic radius of Ba^{2+} in the NBT lattice will create the A-site distortion in the perovskite structure. Four bands are visible around 269 cm^{-1} , 539 cm^{-1} , 613 cm^{-1} and 822 cm^{-1} . The band at 269 cm^{-1} is very sensitive to any structural transitions. It is dominated by A_1 mode vibrations and it corresponds to the vibration of Na-O and Ti-O bonds. The high frequency bands near 539 cm^{-1} and 613 cm^{-1} are well known for the NBT based ceramics are attributed to the vibration of TiO_6 namely stretching and scissoring vibration of oxygen octahedrons. The 822 cm^{-1} band are correlated due to presence of oxygen vacancies, and their intensity yields the vacancy concentration. This region can be linked to the A_1 (LO) and E (LO) overlapping bands. Due to

the high mass of the bismuth atoms, the Bi-O band have present at a very low frequency and was not observed.

Peng du et al. investigates the dielectric, ferroelectric, and the piezoelectric properties in solid solution of (1-x) NBT-x CT. XRD analysis with different concentration from $x=0$ to 0.08. The data shows there is no secondary phase exists. That confirms that Ca^{2+} have diffused into the sample to produce a new sample NBT-CT. When $X < 0.04$ then both lattice parameter c and the lattice volume both increases but above 0.04 it again decreases but at 0.06 it get maximum which means the lattice distortion in the NBT-CT are induced by the polarizing field.

Investigating the dielectric constant as a function of temperature and frequency they found two characteristic temperature *depolarizing temperature* T_d and T_m . In the former one above this temperature there is no piezoelectric response was observed in the NBT-CT ceramic which indicating the transformation of the polar state to the non polar state. Ferroelectric long range orders decreases at above Depolarizing temperature and get the first $\tan\delta$ peak. It was observed that depolarizing temperature decreases with increasing of the concentration of CT (calcium Titanate), when CT content increase from 0 to 0.06 then T_d decreases from 148°C to 34°C . second dielectric anomalies achieved when system attain a new temperature (T_m) where system attain maximum dielectric constant.

In P-E loop measurement it observed at $X=0.06$ attain low remnant polarization with lower coercivity that indicates the decreasing of the anisotropy of the material.

CHAPTER 3

This chapter includes the details about synthesis of NBT-BT and NBT-CT ceramics and different characterization techniques have used to characterize it.

3.1. EXPERIMENTAL TECHNIQUES:-

- (1) Preparation of solid solution of NBT-BT and NBT-CT by solid state reaction process.
- (2) Characterization of the NBT-BT and NBT-CT CERAMICS.

3.2. SYNTHESIS METHOD:-

- (1) Powder preparation
- (2) Grinding
- (3) Powder calcinations
- (4) Pelletization
- (5) Sintering pellet

3.3. CHARECTARIZATION TECHNIQUES:-

- (1) X- ray diffraction
- (2) Raman spectroscopy
- (3) Scanning electron microscopy
- (4) Dielectric study
- (5) P-E loop

3.4. RAW MATERIAL USED FOR SYNTHESIS:-

For NBT-BT THE RAW MATERIALS ARE-

Bi₂O₃ (Bismuth oxide)

Na_2CO_3 (Sodium carbonate)

TiO_2 (Titanium Oxide)

BaCO_3 (Barium carbonate)

For NBT-CT RAW MATERIALS ARE-

Bi_2O_3 (Bismuth oxide)

Na_2CO_3 (Sodium carbonate)

TiO_2 (Titanium Oxide)

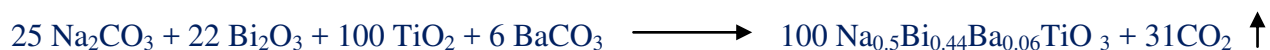
CaCO_3 (calcium carbonate)

3.5. PREPARATION OF POWDER:-

SYNTHEIS OF NBT-BT-

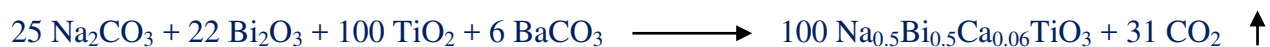
Solid state synthesis route is adopted due to its easiness and precursors are less expensive. The raw materials are weighed in stoichiometric proportion to start by synthesis process.

The chemical equation is-



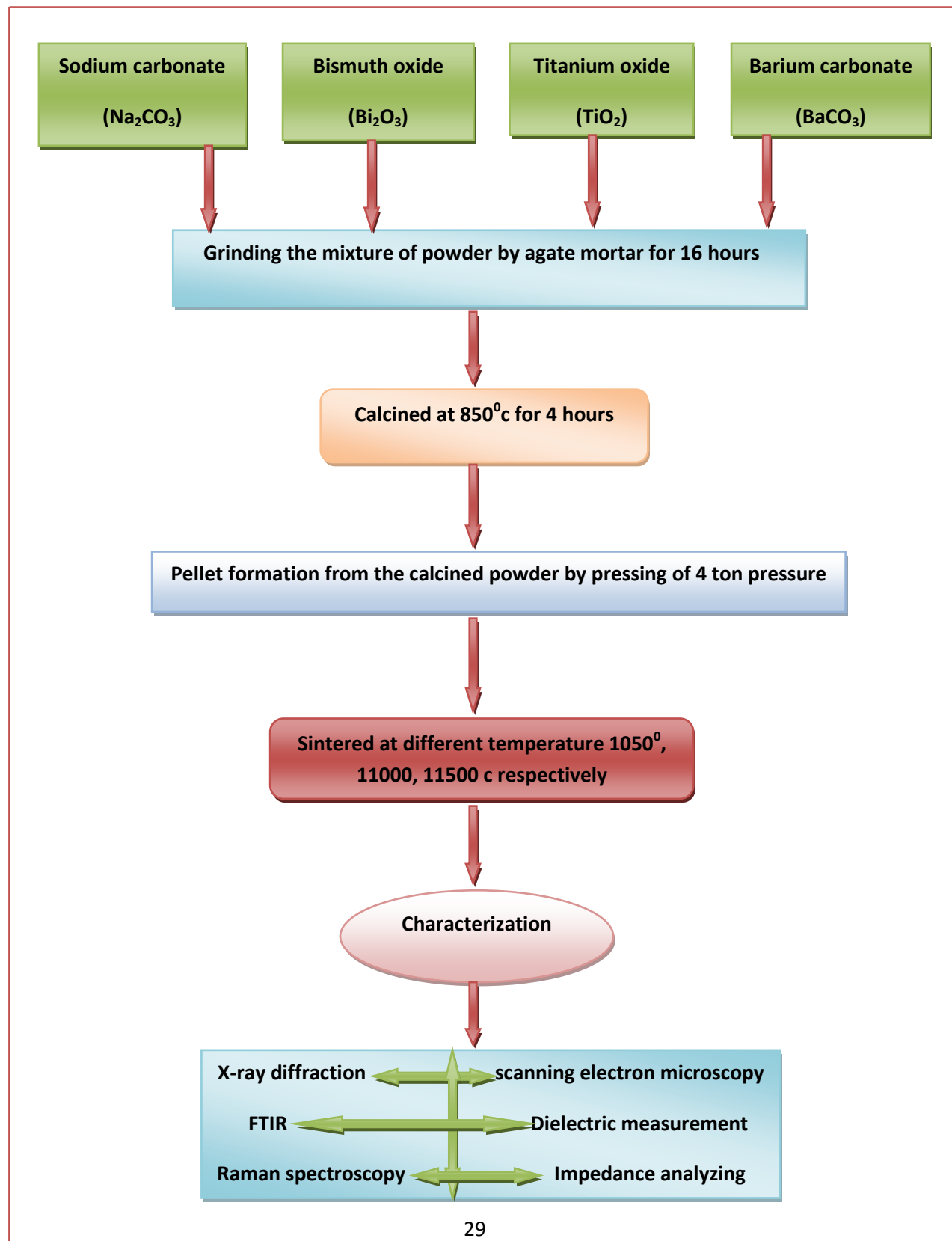
SYNTHESIS OF NBT-CT-

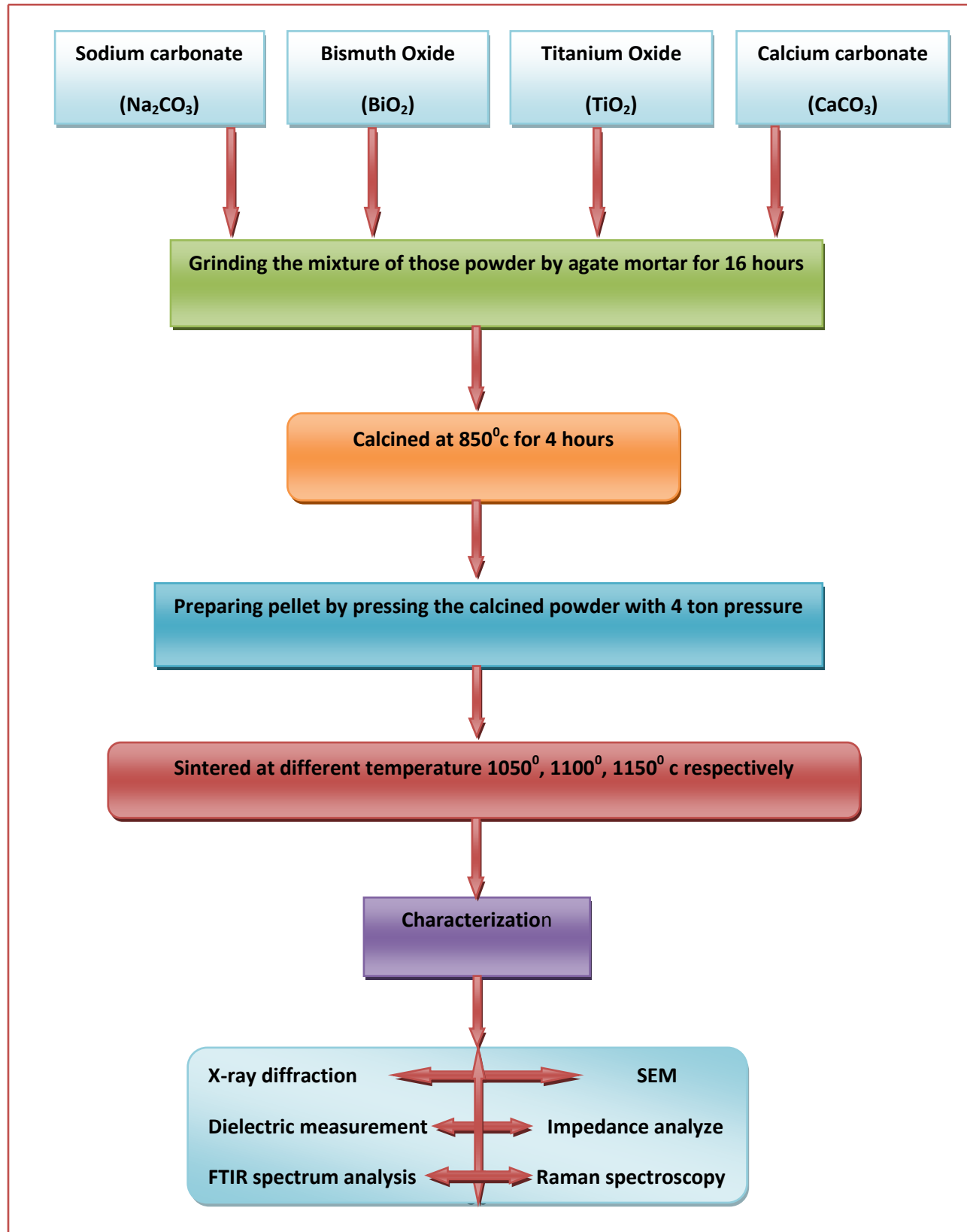
The chemical equation is-



3.7. FLOW CHART OF WORK:-

FLOW CHART FOR PREPARATION OF NBT-BT-



FLOW CHART FOR PREPARATION OF THE NBT-CT-

3.8. EXPLANATION OF DIFFERENT PROCESS USED IN SYNTHESIS:-

3.8.1. CALCINATION:-

It is kind of heat treatment process where in the absence or limited supply of air or oxygen applied to the materials to bring about a thermal decomposition. Calcinations reaction usually takes place at or above the decomposition temperature (for decomposition and volatilization) or the transition temperature (for phase transition) but below the melting point. This temperature is defined as the temperature at which standard Gibbs free energy for a particular calcinations reaction is zero. Here pure NBT-BT is calcined with temperature is about 850 for 2 hours.

3.8.2. PELLET FORMATION:-

The calcined powders of NBT-BT and NBT-CT mixed with 3% polyvinyl alcohol (PVA) binder and had grinded for four hours continuously without any interruption. After drying the sample is scrapped from the agate mortar and separately pellets are prepared by the help of dieset and pelletize under a load of 4 ton.

3.8.3. SINTERING:-

It is also a heat treatment after prepare the pellet again heat the sample with high temperature to obtain a highly dense ceramic system. The reduction of the excess surface energy associated with particle surface is the macroscopic driving force operating during the process. This achieved by two ways- i) reduction of the total surface area by an increasing of the average particle size. ii) The elimination of solid/vapor interface to decrease the Rayleigh-Taylor instability and creation of grain boundary area followed by grain growth which leads to give the densification.

If the atomic process that leads to densification dominates, the pores get smaller and disappear with time. This process is called the Sintering.

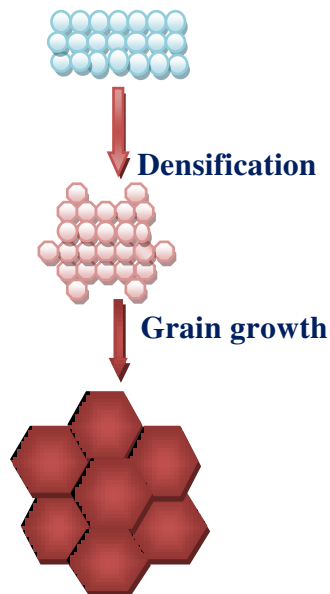


Fig .8. -Picture that shows how the particle lowers their energy at sintering process

Here for NBT-BT and NBT-CT the sintering done for 1050⁰c, 1100⁰c, 1150⁰c for three hours and cooling rate of 5⁰c/min.

3.8.4. X-RAY DIFFRACTION:-

X-ray diffraction is used to do structural analysis of any material. However this experiment is most sensitive to the high Z because linear dependency of the atomic scattering factor on atomic number. Due to angstrom order X-ray wavelength it having the resolution in the sub-angstrom ranges. A one dimensional row of similar atoms having equal inter-atomic spacing can be treated as a infinite grating, if spacing between the atom is in the angstrom range, then irradiation of a beam of monochromatic X-ray can produce the diffraction. The direction of diffraction lines can be accounted for if X-rays are considered to be reflected by such a set of parallel atomic planes followed by the constructive interference of the resulting reflected rays.

If a beam of parallel X-ray impinges on the parallel planes of spacing of 'd' with an angle of ' θ ', then condition of constructive interference is path difference between the two rays shown in the picture equal with integral number(n) of wavelength.

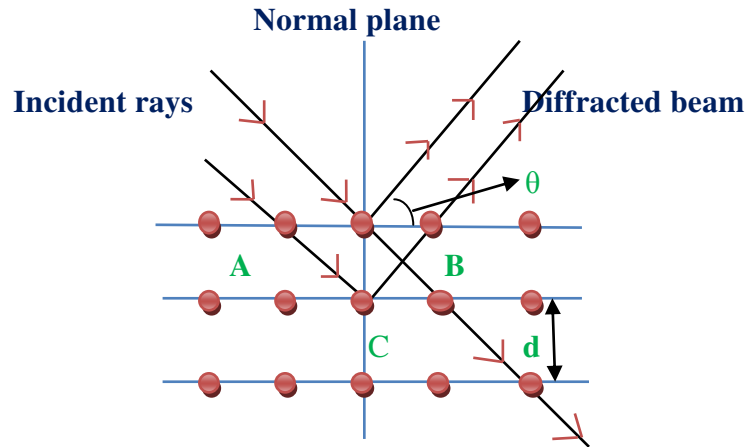


Fig.9. - Bragg's reflection from the set of set of parallel crystal planes with spacing of 'd'

Path difference between two rays = $AC+BC = 2d\sin\theta$ i)

To satisfy the interference condition this path difference should equal with the integer of the wavelength (λ)-

So the Bragg's condition will be,

$$2d\sin\theta = n \lambda \quad \text{.....ii)}$$

Powder XRD method is most widely used method because at the sintering process when material growth is going on then on his way then to decrease the surface energy and the Rayleigh-Taylor instability material produce the grain boundary and grain boundary grooving and to get the extra stability they form polycrystalline state. In the polycrystalline grains are oriented in different direction, when the material is in bulk state then impinging of the X-ray cannot interact with all those grains due to less scattering cross-section. So only possibility is to form fine powder containing a large number of tiny crystallites with random orientation. Then different set of crystallites will be exposed in front of X-ray that leads to give the proper result.

In XRD analysis the splitting of the (200) plane to (002) and (200) confirms the existence of the morphotopical phase boundary between Rhombohedral and the Tetragonal phase.

3.8.5. RAMAN SPECTROSCOPY:-

Raman spectroscopy is the versatile tool to investigate the local structural distortion. The dynamical behavior of the lowest wave number optical mode (Soft mode) has been greatest interest in ferroelectric materials. Raman scattering is very sensitive to subtle structural modification and can be used to detect the low concentration impurity phase which remain unspecified in the normal diffraction methods. A Raman spectrum usually contains the intensity versus difference between the incident and the scattered beam wave number and peaks are related to the corresponding phonon energy. Because of small wave vector of optical photon, the phonons in the Raman scattering of crystalline solids have very small momentum with the Brillouin zone. Therefore only zone centered phonons are participated in the Raman scattering.

Raman studies conducted by the back scattering geometry using a Juvin-Yvon T-6400 triplemate instrument utilizing laser radiation of 514.5 nm from a coherent Innova 99 Argon source. The green light laser was focused in two 2mm by using the Raman microprobe with 50x objective. A charge coupled device (CCD) collected and precede the scattered light. The investigation of the scattered time, slit width and laser beam are adjusted in order to achieve high signal to noise ratio (SNR).

3.8.5. SCANNING ELECTRON MICROSCOPY:-

Scanning electron microscopy (SEM) is basically a type of electron microscopic technology that produces an image of a given sample by scanning it with a focused electron beam. Electrons interact with the sample, and produce various signals that contain information about the sample's surface morphology and the composition. Here beam position is combined with the detected signal to produce an image. SEM can attain resolution up to nanometer range. Process should do in high vacuum otherwise instead of interacting with the sample electron beam will interact with the air particle that gives low resolution.

Most common SEM mode is to detect the secondary electrons emitted from an atom by the influence of electron beam. By scanning the sample and collecting the secondary electrons coming from the sample detect by some special detector, and an image displaying on the surface is created. Signal result from the interaction of the e-beam with various atom with different depths within the sample. Most popular detection mode is secondary electron imaging where electrons are coming very close from the surface that gives proper surface topography. It is more sensitive with high atomic number atom (Z). Resolution of an image depends on to the spot size, due to narrow electron beam, SEM micrograph having high resolution. SEM having more than 50,000 times resolution than optical microscopes. SEM images of the pure NBT-BT and the NBT-CT ceramics has shown in fig.13. and fig.14. respectively. The grains of both samples were well developed at various sintering temperature 1050°C , 1100°C , and 1150°C respectively. The grains of the NBT-BT and NBT-CT ceramics have dense structure, which are similar to that of the typical NBT-BT and NBT-CT ceramics. With increasing temperature grains shape changes from granular like grains to plated grains. SEM image confirms that grain growth and stacking are more at high temperature. But due to Rayleigh-Taylor instability non-uniform grains are formed.

3.8.6. IMPEDANCE ANALYZING:-

For piezoelectric material impedance analyzing is another tool to characterize electrical properties. The variation of the impedance can be analyze by drawing the equivalent circuit for electrical circuit having two parallel/series component impedance shown below-

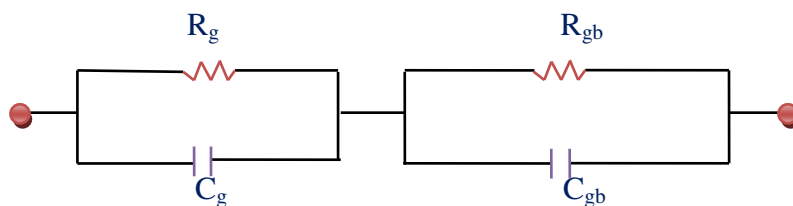


Fig.10. - Equivalent circuit model

Where

R_g be the grain resistance and R_{gb} is the grain boundary resistance and C_g and C_{gb} be the grain and grain boundary capacitance.

$$\text{Impedance (Z)} = Z' - j Z''$$

Where

Real impedance (Z') = $Z \cos\theta$ and imaginary impedance (Z'') = $Z \sin\theta$, ' θ ' define phase factor.

And the plot of imaginary and real impedance give two semicircle loop, where first loop stands for the grain boundary resistance and later one stand for the grain resistance. By doing temperature and the frequency dependency of the impedance value one can interpret the nature of the material.

3.8.7. DIELECTRIC MEASUREMENT:-

Piezoelectric materials are basically dielectrics. So to characterize any dielectric species need to do dielectric constant, loss tangent factor, impedance measurement. The temperature dependence of dielectric constant and loss tangent factor introduce vital information about the phase transition. Generally this measurement performed in parallel plate capacitor configuration. Suppose a parallel capacitor is filled with a dielectric material then its capacitance will change, and more when apply electric field with alternating electromotive force ε with frequency of ω and an alternating current ' i ' flows through the capacitor.

$$i = j\omega\varepsilon_r C_0 \varepsilon$$

Where, C_0 is the capacitance of the parallel capacitor, ε is the relative permittivity of the sample having frequency dependency, ω is the frequency.

As there are leakage current issues then relative permittivity is no real it is now transformed to an imaginary number

$$\varepsilon^* = \varepsilon'(\omega) - j\varepsilon''(\omega)$$

Where $\epsilon'(\omega)$ represent the real term of the dielectric constant and $\epsilon''(\omega)$ represent the imaginary term $\tan\delta$ represent the dielectric loss of the sample. Loss tangent normally defined as the ratio of imaginary dielectric constant to real dielectric constant.

$$\tan\delta = \epsilon''(\omega) / \epsilon'(\omega)$$

For the leakage issue dielectric impedance also becomes imaginary,

$$Z = Z' + j Z''$$

Where, Z' is the real part of the impedance and Z'' is the imaginary part of the impedance,

With $Z' = Z \cos(\theta)$ and $Z'' = Z \sin(\theta)$

Where

' θ ' is the phase factor.

CHAPTER 4

➤ RESULT AND DISCUSSION:-

This chapter covers all the result that we did to characterize the sample with discussion.

4.1. XRD DATA ANALYSIS:-

We did our experiment with and XRD scanning angle 20° to 90° with 0.017 step size for 1 hour per sample. Fig.11., Fig.12. represent the XRD pattern for NBT-BT and NBT-CT for sintering temperature 1100°C , 1150°C respectively. However the grain growth at $<900^{\circ}\text{C}$ is not so obvious that why we select above temperature for our investigation purpose. At different temperature we get almost same result but having different intensities with different temperature. Intensity of the XRD pattern increase with sintering temperature that conclude that at higher sintering temperature densification is more so as a result scattering will be more as we know number of scattering defines the intensity. So the increasing of intensity with increasing of sintering temperature concludes the densification of the sample. From XRD peak analysis (111) peak splitting indicate the existence of Rhombohedral phase while (200) peak splitting give rise to indicate the existence of tetragonal phase so there exist a morphological phase boundary between Rhombohedral and tetragonal phase for NBT-BT and Rhombohedral and octahedral for NBT-CT respectively. We observed peaks are shifted towards left due to doping of Barium and towards right due to the doping of Calcium due to the difference size between the dopants from the A-site ion ($\text{Ca}^{2+}=1.34\text{\AA}^0$, $\text{Na}^{+}=1.39\text{\AA}^0$, $\text{Bi}^{3+}=1.30\text{\AA}^0$, $\text{Ba}^{2+}=1.42\text{\AA}^0$), which indicate due to Barium NBT crystal structure become lengthened and due to Calcium doping crystal become shrinks because of the *Off centering ion effect*.

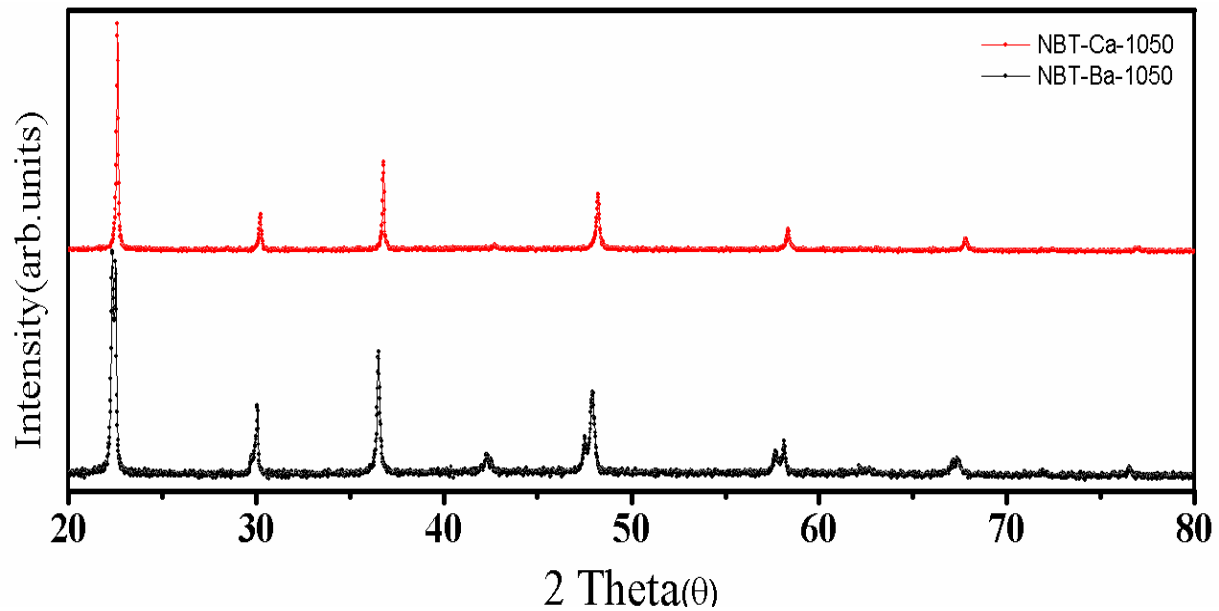


Fig.11. - Shows XRD data for NBT-BT and NBT-CT for 1050⁰c which shows morphotropical phase boundary in those ceramics

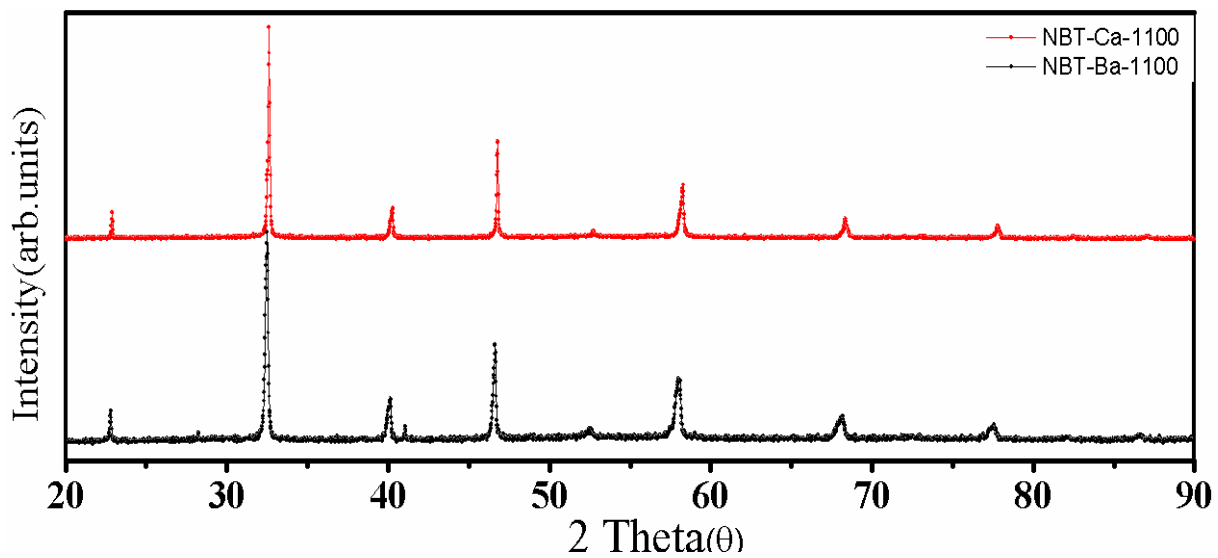


Fig.12. - Shows the XRD data of NBT-BT and NBT-CT for 1100⁰c which shows morphotropic phase boundary in the ceramics.

4.2. SEM ANALYSIS:-

SEM analysis of both samples has shown in the Fig.13. Fig.14. at different temperature 1050⁰c, 1100⁰c, 1150⁰c respectively to understand the grain growth phenomenon of our sample NBT-BT and NBT-CT with increasing temperature. From fig it is well understood that grain growth are happening with the increasing temperature. Because at 1100⁰c the whickers are starts to get thinner in the vicinity of the grain boundaries showing grain boundary grooving as a result of surface to grain boundary diffusion. The system has unusually higher grain boundary energy as compared to the surface energy. As a result, on further heating at 1150⁰c the whickers eventually disintegrate into individual grains due to minimize the Rayleigh-Taylor instability. So grain boundary energy is minimized by thermal grooving to achieve an equilibrium cubical shape of grain. The grain boundary grooving and Rayleigh-Taylor instability both leads to disintegrate the bamboo shaped structure to cubic grain structure to get the thermal stability to minimize the surface energy. When sintering temperature increases then some thermal perturbation has generated but with increasing of temperature this perturbation growth with exponentially that gives the nonlinearity inside the sample that is why at low temperature grain sizes are almost non-linear but at higher temperature due to obtain thermal stability, grain growth are much more linear.

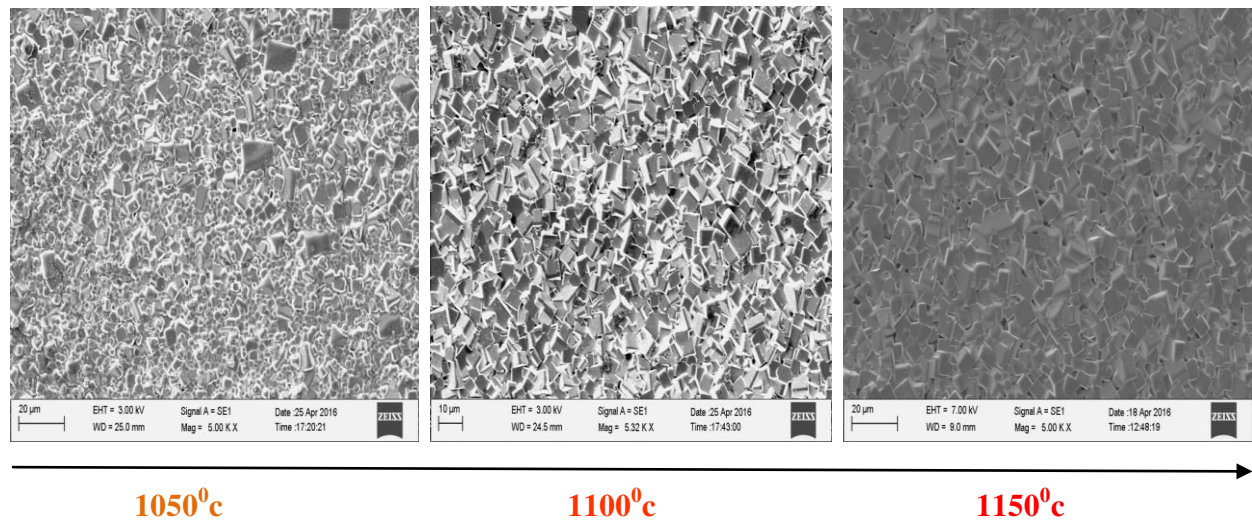


Fig.13. - SEM image for NBT-BT indicate the grain growth with different sintering temperature 1050⁰c, 1100⁰c, 1150⁰c respectively.

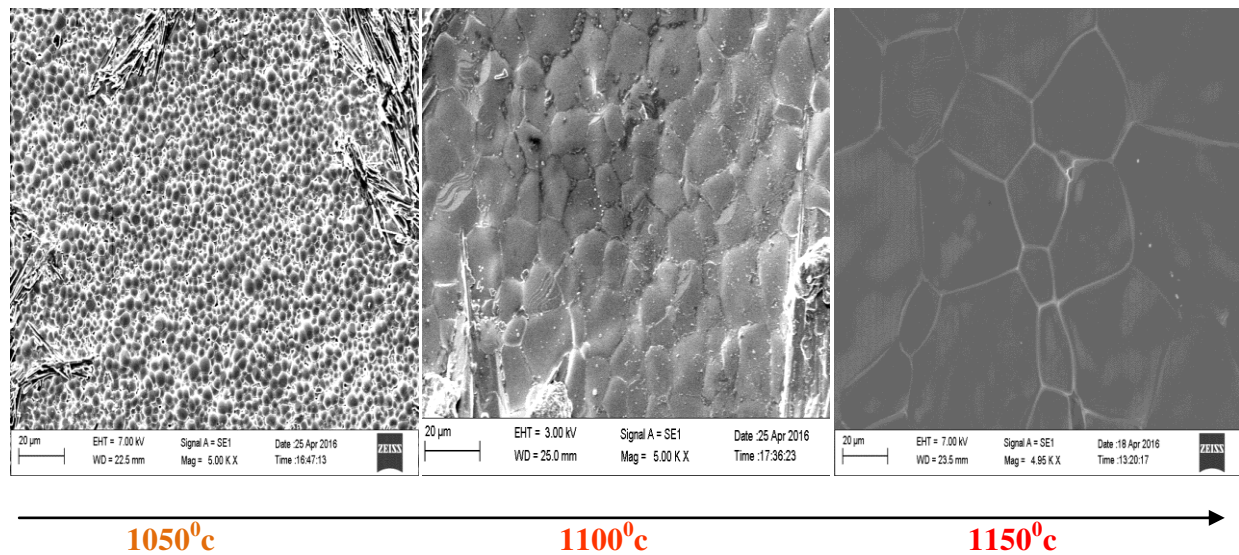


Fig.14. - SEM image for NBT-CT indicate the grain growth with different sintering temperature 1050⁰c, 1100⁰c, 1150⁰c respectively.

4.3. RAMAN SPECTROSCOPY:-

We did Raman spectroscopy for both sample NBT-BT and NBT-CT which shown in Fig.15. The atomic mass of both Ba^{2+} and Ca^{2+} is in between the Na^+ and Bi^{3+} and the ionic radius is large compared to the Na^+ . So the substitution of Ba^{2+} in the NBT matrix creates the A-site distortion those are clearly visible from the peaks. Four bands are clearly visible around 137 cm^{-1} , 271 cm^{-1} and 539 cm^{-1} , 788 cm^{-1} for NBT-CT. The band at 137 cm^{-1} is very sensitive to any structural transition. It is dominated by the A_1 mode vibration corresponds to the vibration of Na-O and Ti-O bonds. High frequency bands near 271 cm^{-1} , 539 cm^{-1} are well known for the NBT based ceramics and attributed to the vibration of TiO_6 namely stretching and scissoring vibration of oxygen octahedrons. The 788 cm^{-1} bands are correlated to the presence of vacancies and their gives the vacancy concentration.

Four bands are also clearly visible around 111 cm^{-1} , 272 cm^{-1} and 541 cm^{-1} , 759 cm^{-1} for NBT-BT. The band at 111 cm^{-1} is very sensitive to any structural transition. It is dominated by the A_1 mode vibration corresponds to the vibration of Na-O and Ti-O bonds. High frequency bands near 272 cm^{-1} , 541 cm^{-1} are well known for the NBT based ceramics and attributed to the vibration of TiO_6 namely stretching and scissoring vibration of oxygen octahedrons. The 759 cm^{-1} bands are correlated to the presence of vacancies and their gives the vacancy concentration.

Due to high mass of the Bi atom, the Bi-O will fall at very low frequency and was not observed in our experimental condition. Raman pattern shows irregularity and roughness due to the data taken at the high resolution. But to neglect the problem if one takes the data, it is impossible to distinguish the closely bounded molecule.

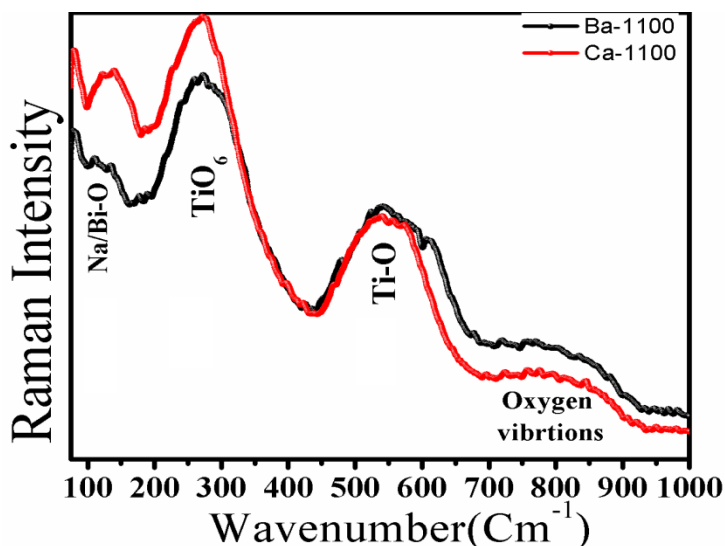


Fig.15. - Raman spectrum of NBT-BT and NBT-CT

4.4. FTIR SPECTRUM ANALYSIS:-

FTIR spectrum of both NBT-BT and NBT-CT is recorded at room temperature from 400cm^{-1} to 4000 cm^{-1} and is shown in Fig.16. The bands at 713cm^{-1} and 941cm^{-1} are corresponds to the bending vibration of Bi-O units in $[\text{BiO}_3]$ and $[\text{BiO}_6]$ polyhedral units respectively and this vibration may be assigned the inter-polyhedral vibration and the presence of bands at 2362cm^{-1} , 2978cm^{-1} are due to the stretching vibration of BaO_6 and TiO_6 in NBT-BT structure for NBT-CT the bands at 708cm^{-1} and 950cm^{-1} are corresponds to the bending vibration of Bi-O units in $[\text{BiO}_3]$ and $[\text{BiO}_6]$ polyhedral units respectively and this vibration may be assigned the inter-polyhedral vibration and the presence of bands at 2365cm^{-1} , 2969cm^{-1} are due to the stretching vibration of CaO_6 and TiO_6 in NBT-CT structure and this asymmetry stretching vibration changes in bond length of Ti-O bond along the crystallographic angle and confirms the presence of oxygen group.

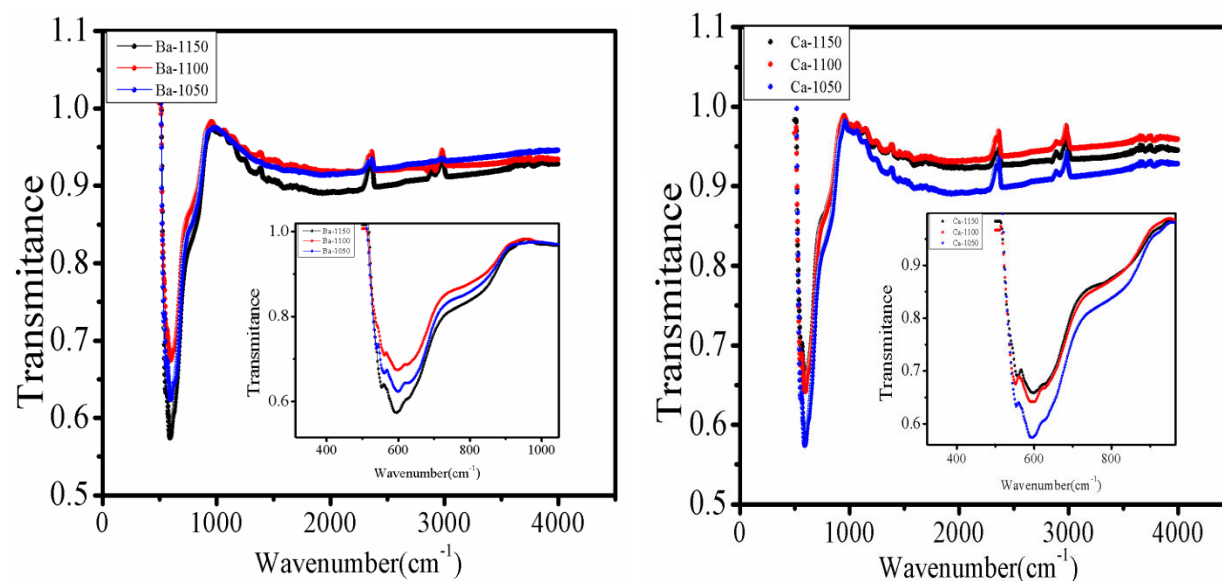


Fig.16. - FTIR spectrum for NBT-BT and NBT-CT at different temperature.

4.5. DIELECTRIC MEASUREMENT:-

Fig.17. shows the dependency of dielectric constant with temperature and the driving frequency. High dielectric constant value describes the existence of the morphotropical phase boundary. There are two temperatures where the dielectric anomalies take place. At depolarizing temperature (T_d) long order ferroelectric properties go down as a result it shows the relaxor behavior. At (T_m) dielectric constant increase again .With increasing of temperature again it attains a maximum value where polar to non polar phase transition has takes place with first order phase transition that gives rise to produce high dielectric constant at that point called the curie temperature(T_c).

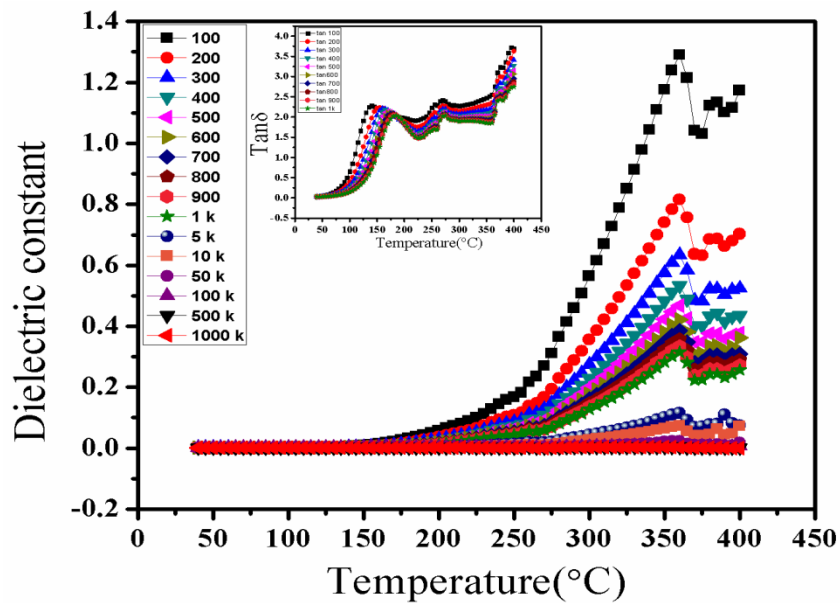


Fig.17. - Dielectric and loss tangent measurement at different temperature and frequency

4.6. IMPEDANCE ANALYSIS:-

We did impedance analyzing for both sample NBT-BT and NBT-CT where Behavior of Real impedance and imaginary impedance of NBT-CT at different temperature and frequency is shown in Fig.18 and variation of Real impedance with imaginary impedance in Fig.19. and we observe real and imaginary both impedances decreases with the increasing of temperature which may be due to the release of space charge as a result reduction of barrier energy which is responsible for the enhancement for the conductivity which decrease the impedance. Also at the low frequency with increasing of the temperature impedance has also decrease.

At high frequency charging and discharging are going faster which decrease the charge carrier density on the capacitor plate and also increase leakage current, which leads to degrade the capacitance with frequency. Electrical modulus and the capacitance are shown in the Fig.19. and Fig.20. From the imaginary electrical modulus there are two parts- a) at the low frequency part peak represent range of the frequency where charge carriers are mobile over long distance. b) higher frequency side of imaginary impedance (M'') peak represent the range of frequency in which the ions are spatially confined to their potential well their ions can make only short range motion within the well.

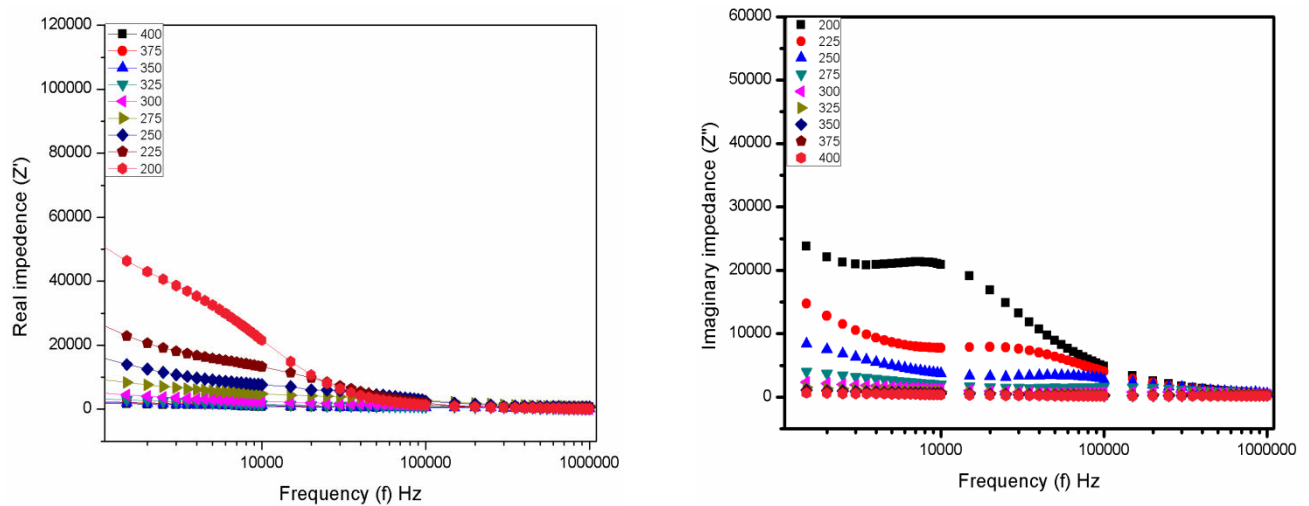


Fig.18. - Behavior of Real impedance and imaginary impedance of NBT-CT at different temperature and frequency

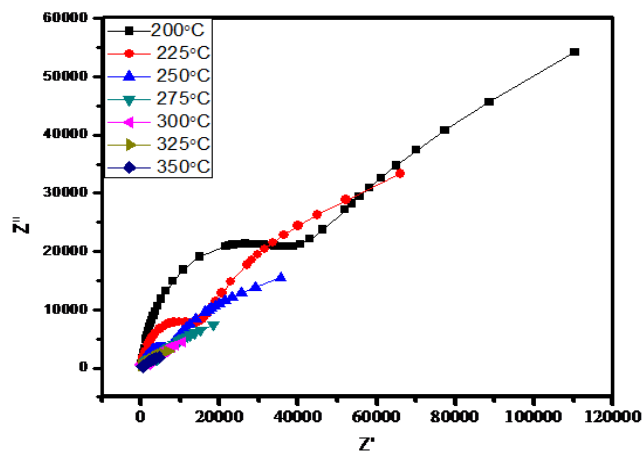


Fig.19. - variation of Real impedance with imaginary impedance which gives grain boundary resistance and grain resistance corresponds to two semicircular peaks respectively

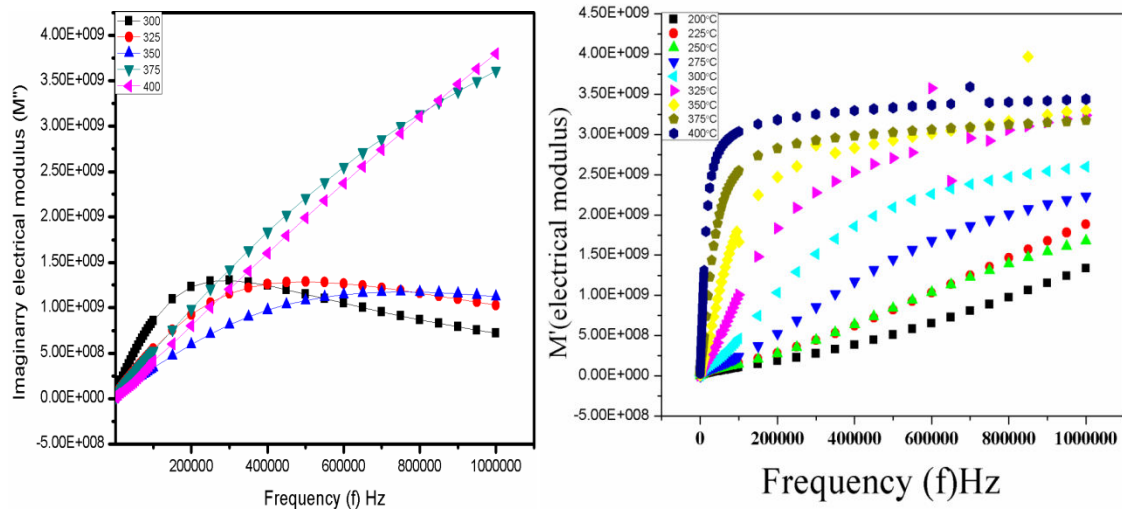


Fig.20. - Behavior of the imaginary and real electrical modulus for NBT-CT at different temperature and frequency.

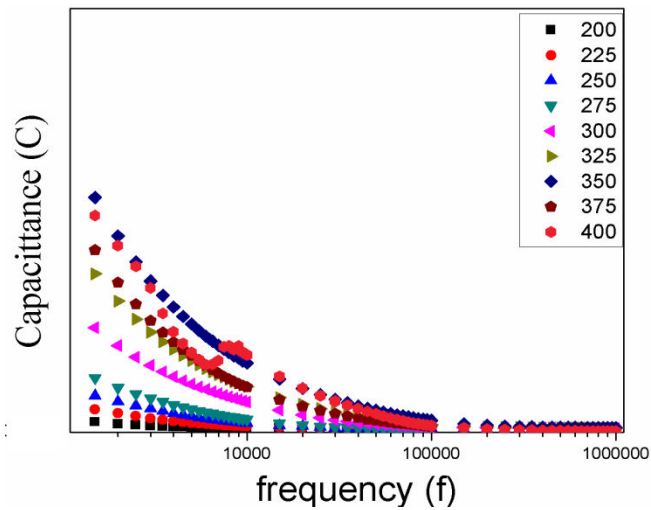


Fig.21. - Capacitance of the NBT-CT sample at different temperature and frequency

CHAPTER 5

➤ CONCLUSION:-

- i) Splitting of the peaks in XRD pattern indicates the existence of morph tropical phase boundary of $(1-x)\text{NBT} - x \text{BT}$ and $(1-x)\text{NBT} - x \text{CT}$ with concentration of $x=0.06$, which gives more prominent dielectric property.
- ii) Raman pattern shows the vibration of Na-O and Ti-O bonds with some roughness or irregularity due to the data taken in high resolution. Bands are also correlated the presence of oxygen vacancies and vacancy concentration inside the sample which made the A-site disorder.
- iii) SEM image shows that with increasing sintering temperature grain growth is much proper and regular also.
- iv) FTIR spectrum confirms the asymmetric stretching of Bi-O and Ti-O due to presence of oxygen which also shown in Raman pattern.
- v) Dielectric study shows two characteristic temperatures T_d and T_m which gives the dielectric anomalies.
- vi) Decreasing of real and the imaginary value of the impedance conclude the release of space charge which enhance the conductance by decrease the potential barrier as a result impedance of the system decreases. Variation of imaginary impedance with real impedance gives two semi-circular peaks which correspond to the grain boundary and grain resistance respectively.
- vii) Variation of electrical modulus gives the reason of movement of charge carrier in different condition/situation with respect to different temperature.

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