

A
Thesis
On
**SYNTHESIS AND CHARACTERIZATIONS OF BNT-BT
AND BNT-KNN CERAMICS**

By

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Under the Supervision

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Certificate from the Supervisor

This is to certify that the thesis entitled, “SYNTHESIS AND CHARACTERIZATIONS OF BNT-BT AND BNT-KNN CERAMICS” prepared by **Ms. SUSHREE SANGEETA BARIK**, Roll No: 412PH2088 of Department of Physics of **National Institute of Technology, Rourkela**, for the partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN PHYSICS, at NIT, Rourkela**, is absolutely based upon the research work carried out by her under my supervision and guidance.

To the best of my knowledge, these results have not been submitted by her for the award of any other degree or diploma.

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ABSTRACT

BNT-BT $[(0.93\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 - 0.07\text{Ba-TiO}_3]$ and BNT-KNN $[(0.93\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 - 0.07\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3]$ was prepared by the solid state route using microwave process. The prepared sample was calcined at 900°C for 10 minutes by microwave process for both BNT-BT and BNT-KNN. Then the sample was characterized by different techniques, from XRD of the sample a single perovskite phase was confirmed. All the samples were sintered using the microwave sintering method at 1150°C for 30 minutes with a heating rate of $40^\circ/\text{min}$. The FE-SEM micrograph images of the samples showed dense microstructure and uniform grain size. Then the study of dielectric properties of the sample was done. The P-E loop measurement confirms the ferroelectric nature of the sample.

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1. INTRODUCTION TO DIELECTRIC AND FERROELECTRICS

Recently the advances in ceramic technology have brought about a tremendous revolution in the world. A lot of researches in the field of dielectrics have done to improve its application in a huge area. Most of the ferroelectrics are dielectrics. In order to understand the properties of ferroelectrics we need to understand what is dielectric and what are the properties of dielectrics.

1.1 DIELECTRICS

Dielectric materials are insulators in which by the application of electric field polarization occurs. In contrary to the conductors electric charges don't flow through the dielectric material when placed in an electric field but shift from their average equilibrium position causing polarization. The amount of polarization caused can be explained by dielectric constant ϵ_r .

1.1.1 POLARIZATION

When dielectrics are placed in an electric field, the positive and negative charges are displaced from their equilibrium positions by a very small distance. This in turn causes in the formation of large no. of dipoles each having some dipole moment in the direction of the field which is called polarization [1]. The polarization can be calculated by dipole moment per unit volume.

TYPES OF POLARIZATION

1. ELECTRONIC POLARIZATION

In this type of polarization the electron cloud of an atom displaces from its nucleus in the presence of an applied electric field. At optical frequency range the polarization and dielectric constant results from electronic polarization. It is temperature independent large atoms have a large electronic polarizability.

2. IONIC POLARIZATION

It is observed in the ionic crystals and arises due to displacement of a charged ion relative to other ions in a solid under applied electric field.

3. DIPOLAR POLARIZATION

Dipolar polarization arises due to polar substances which orient themselves in the presence of an external electric field. At ambient temperature, all the dipole moments have statistical distribution of their directions.

4. SPACE CHARGE POLARIZATION

This type of polarization exists in dielectric materials which show spatial inhomogeneities of charge carrier densities. It arises due to accumulation of charges at the interface or at the grain boundary of a polycrystalline material and diffuses over appreciable distances with the applied electric field.

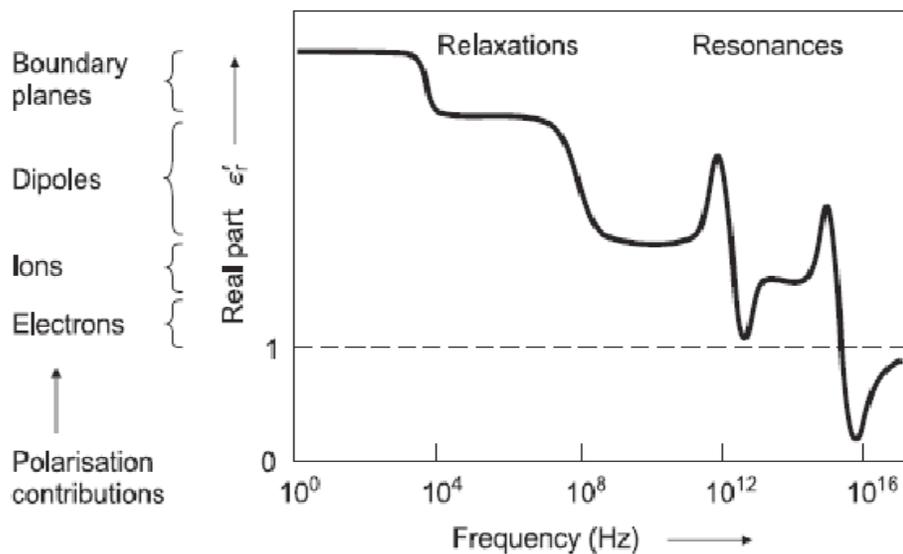


Figure 1. Shows the variation of polarization with frequency

1.1.2 DIELECTRIC RELAXATION

In order to reach maximum value of polarization dielectrics takes finite value and this is due to the forces between adjacent molecules which tend to prevent the alignment along the external field. This phenomenon is named as dielectric relaxation. It is an inherent property of a relaxor ferroelectric.

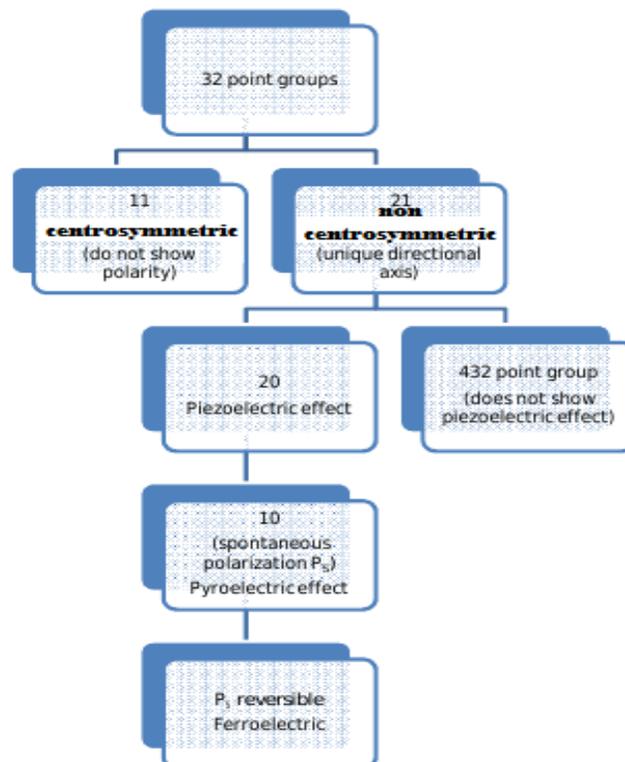
1.2 FERROELECTRICS

Ferroelectricity was initially discovered by Valasek in Rochelle salt. Most ferroelectric are dielectric materials that show spontaneous polarization when cooled below Curie temperature even in the absent of electric field. The centers of positive and negative charges never coincide in ferroelectric crystal [2]. The polarization versus electric field plot for a ferroelectric crystal shows a hysteresis loop in contrary to linear dielectric which doesn't show hysteresis. It is in fact one of the obvious cause that makes the study of dielectrics such a popular field.

1.3 PROPERTIES OF FERROELECTRICS

1.3.1 CRYSTALL SYMMETRY

Every crystal can be described by the 230 crystallographic space groups and 32 point groups [3,4]. The classification is shown below



1.3.2 PIEZOELECTRIC EFFECT

The word piezoelectricity is derived from the Greek letter word pieze / piezein that means to squeeze or to press and electric stands for a source of electric charge. Piezoelectric effect arises due to the development of electric charge on the surface of a crystal when a mechanical stress is applied which means mechanical deformation is produced on application of an electric field. Non centrosymmetry crystal normally exhibits this effect [5]. In order to produce piezoelectric effect, a very strong electric field is applied which results in the dipoles facing nearly the same direction.

1.3.3 SPONTANEOUS POLARIZATION AND PYROELECTRIC EFFECT

Spontaneous polarization can be described by the value of dipole moment per unit volume. And also can be given by the value of charge per unit area on the surface perpendicular to the axis of spontaneous polarization. Crystals having unique polar axis show a spontaneous polarization vector P_s along the axis. Spontaneous polarization is temperature dependent. When spontaneous polarization occurs due to change in temperature is called pyroelectric effect. The word pyroelectricity is derived from the Greek word “pyr” that means fire. This phenomenon was first discovered by Tourmaline crystal theophrast in 314 BC. and was named so by Brewster in 1824.

$$\Delta P_s = P \cdot \Delta T$$

Where P = pyroelectric coefficient

ΔT = small change in temperature

ΔP_s = Small change in spontaneous polarization

1.3.4 P-E HYSTERESIS LOOP – AN IMPORTANT CHARACTERISTICS FOR FERROELECTRICITY

Ferroelectric behavior results in a crystal when the magnitude and direction of the spontaneous polarization vector P_s can be reversed by the application of an external electric field. All the ferroelectrics show pyroelectricity where as converse is not true, for example tourmaline shows pyroelectricity but it is not ferroelectric. The tendency of orientation of dipoles in the field direction even in the absence of external electric field can be explained by ferroelectric domains. Domains are separated from one another by interfaces known as domain walls. Electric field causes motion of the domain walls where a very strong electric field may result in the polarization reversal and called “ domain switching” [6,7].

The difference between pyroelectric and ferroelectrics is that the direction of spontaneous polarization can be reversed in ferroelectric materials which can be shown in hysteresis loop.

When electric field increases the domains get align in the direction of the applied electric field so polarization increases. The polarization reaches a saturation value at some high value of field. But when the external field is removed, the polarization doesn't drop to zero and shows remnant polarization P_r . When field is applied in the negative direction of magnitude OF it shows complete depolarization. This negative field is called coercive field strength E_c .

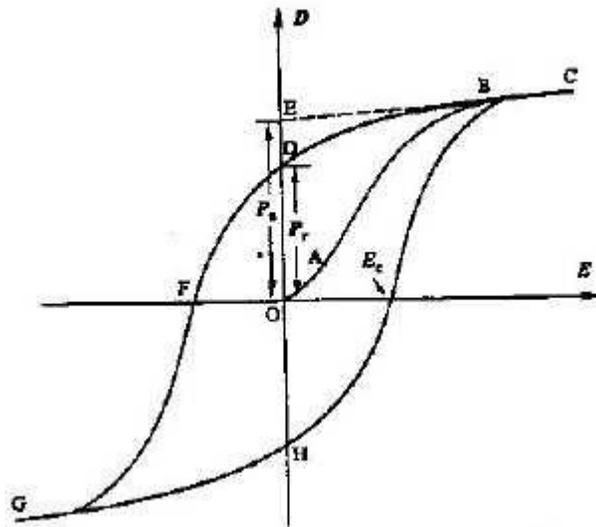


Figure 3.shows the P-E Hysteresis loop

1.3.5 FERROELECTRIC CURIE TEMPERATURE AND PHASE TRANSITION

All the ferroelectric materials must have a transition temperature called Curie temperature (T_c). At Curie temperature the material loses spontaneous polarization and at a temperature $T > T_c$ the crystal doesn't exhibit ferroelectricity but for $T < T_c$ the crystal exhibits ferroelectricity. When temperature decreases across Curie point a ferroelectric crystal undergoes a phase transition from a non-ferroelectric phase to ferroelectric phase. If more ferroelectric phases are present there, then the temperature at which the crystal changes from one ferroelectric to other is known as transition temperature [8]. The temperature dependence of the dielectric constant above the Curie point ($T > T_c$) in ferroelectric crystals can be stated by the Curie Weiss law.

$$\epsilon_r = \epsilon_0 + C / (T - T_0)$$

Where ϵ_r = is the permittivity of the material

ϵ_0 = is the permittivity of the vacuum

C = is the Curie constant

$T_0 =$ is the curie temperature

1.3.6 TYPES OF FERROELECTRICS

Ferroelectric crystals on the basis of transition can be classified under two types displacive or order – disorder. They can also be classified as normal or relaxor ferroelectrics depending upon frequency of ϵ_r . And ferroelectrics are grouped under four main structures. In corner sharing octahedral most of the ferroelectric crystal are made up of mixed oxides containing corner sharing octahedral of O^{2-} ions having cation B inside each octahedron and the space between octahedral are occupied by A ions. The geometric centers of A, B and O^{2-} coincide giving rise to non-polar lattice. The corner sharing octahedral includes perovskites, tungsten bronze type, Bismuth oxide layer structured compounds and pyrochlore. Here we only discuss about perovskite structure.

PEROVSKITE

The Perovskite is a family name of a group of materials. Many piezoelectric (including ferroelectric) ceramics such as Barium Titanate ($BaTiO_3$), Lead Titanate ($PbTiO_3$), Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), Lead Magnesium Niobate (PMN), Potassium Niobate ($KNbO_3$), Potassium Sodium Niobate ($K_xNa_{1-x}NbO_3$), and Potassium Tantalate Niobate ($K(Ta_xNb_{1-x})O_3$) have a perovskite type structure. Some of these ceramics are explained with their properties.

BNT (bismuth sodium titanate):

$Bi_{0.5}Na_{0.5}TiO_3$ (BNT) is one of the ferroelectric perovskite compounds having 1:1 ratio of two different ions $Na_{0.5}$ and $Bi_{0.5}$ at the A-sites. Standardized ABO_3 perovskite formula for BNT is $(Bi_{0.5}Na_{0.5})TiO_3$. An ABO_3 perovskite can be explained 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 hence forming octahedra, and a titanium cation in the center of the oxygen octahedron and another way is a three-dimensional cubic network of 8 corner-sharing TiO_6 octahedra with bismuth and sodium cations at the center of the cube formed by the octahedra. At room temperature, BNT is ferroelectric which passes into an antiferroelectric phase at 473 K and to a paraelectric cubic phase at 593 K. At room temperature BNT has a rhombohedral symmetry with space group $R3c$ which allows for a possible

morphotropic phase boundary (MPB) when mixed with a perovskite-type ferroelectric of tetragonal or orthorhombic symmetry, such as bismuth potassium titanate (BKT), barium titanate (BT), sodium niobate (NN), or potassium sodium niobate (KNN).

Important properties of BNT-

Remnant polarization- $38\mu\text{C}/\text{cm}^2$

Coercive field- 73 kV/cm

Piezoelectric coefficient (d_{33}) –196

Curie point- 320 °C

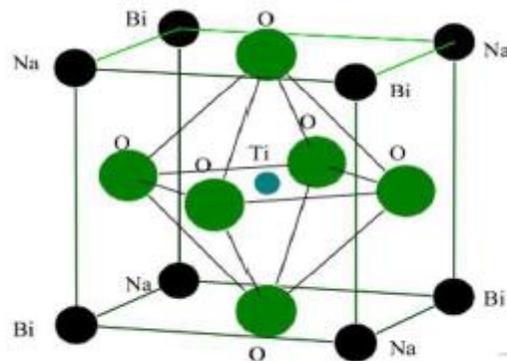


Figure 4. Representation of ABO_3 perovskite shown in cubic BNT

BaTiO₃ (Barium Titanate):-

BaTiO₃ has a perovskite crystal structure and above Curie temperature (about 130°C), it becomes cubic in shape with Ba^{2+} ions at the vertices, O^{2-} ion in the face center position and Ti^{4+} ion in a body-centered position. BaTiO₃ shows the property of polymorphism and above Curie point the lattice structure of the unit cell is cubic whereas below this Curie point the structure starts distorting and changes from cubic to the tetragonal with the orientation of dipole moment. Other transformations occur at temperature close to 0°C and -80°C, below 0°C the unit cell is orthorhombic and below -80°C it shows rhombohedral structure with polar axis along body diagonal. In this case, polarization occurs as a result of the unit shift of axially elongated Ti^{4+} ion crystal. This type of polarization occurs without any application of external electric field or pressure. As it shows spontaneous polarization hence BaTiO₃ is a well-known ferroelectric material and also a good piezoelectric material having excellent dielectric properties. It has

wide application as a dielectric in MLCC (Multilayered Ceramic Capacitor) due to its high dielectric constant and low losses.

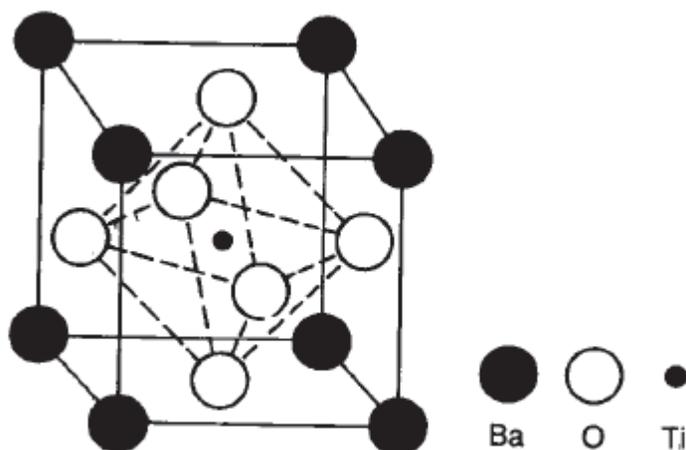


Figure 5. A cubic ABO₃ (BaTiO₃) perovskite-type unit cell

KNN (potassium sodium niobate)

Potassium sodium niobate, $K_xNa_{1-x}NbO_3$ (abbreviated as KNN), is a very good candidate to replace PZT family because of its high Curie temperature and good piezoelectric properties. Potassium sodium niobate is a solid solution of $NaNbO_3$ and $KNbO_3$. The addition of KN to NN results in a ferroelectric phase with a high T_c (exceeding 400°C) and is associated with a decrease in critical electric field needed to induce a ferroelectric phase transition as compared to that of pure NN. KNN is a ferroelectric system with a complex perovskite structure. In this case complex refers to the fact that the A-site is shared by more than one type of ion. KNN is a mixed system of orthorhombic ferroelectric potassium niobate (KN) displaying similar phase transitions to barium titanate but at higher temperatures and orthorhombic sodium niobate (NN), which was originally reported as ferroelectric but is in fact antiferroelectric. NKN was first reported as ferroelectric by Shirane et al.

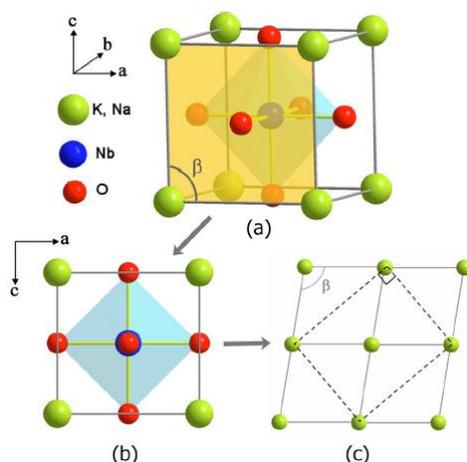


Figure 6 shows structure of KNN

2. LITERATURE REVIEW

2.1 Microwave processing

Among various methods of sintering microwave processing is a relatively new development in material processing [9]. The primary advantage of microwave processing as compared to the conventional techniques is its ability to couple energy directly to the material i.e. energy is supplied by an electromagnetic field to the material through molecular interaction which in turn results in rapid heating throughout the material thickness with reduced thermal gradients. Many of the researchers reported, microwave effects related to both processing of ceramic and polymeric composites. Microwave process has wide application in manufacturing ceramic and polymeric materials which has the potential to improve the quality and reduce manufacturing cost.

Microwave energy applied to the processing or sintering of ceramics, metals and composites gives several advantages over conventional heating method such as unique microstructure and properties, a improved product yield, energy savings, reduction in manufacturing cost and synthesis of new materials [10]. Microwave processing is the transfer of electromagnetic energy and is a energy conversion process rather than heat transfer which occur in conventional heating.

Sutton 1989 reported that the interaction of microwaves with dielectric materials result in translational motions of free or bound charges and rotation of the dipoles. Induced motion is opposed due to inertial, elastic and frictional forces cause losses resulting in volumetric heating. Hence the technology is commercially used for dry application.

Sutton in 1989; Leonelli et al. 2004 showed that selective heating has been widely utilized for the binder burn out purposes during the processing of the green ceramics.

Fang et al(1992,1994 and 1995) showed that hydroxyapatite ceramics were sintered in microwave with significant time and energy saving . It is also shown by him that for transparent hydroxyapatite, the total processing time from start to finish of the sintering process was nearly 20 minute for microwave sintering while it is about 4 hr in the case of conventional sintering.

2.2 Why BNT doped with BT and KNN:-

Now a day an important family of functional ferroelectric material has been highlighted for integration with microelectro mechanical system (MEMS) because of their piezoelectric and pyroelectric properties. At present lead zirconate titanate is the most popular ferroelectric ceramic due to its excellent

piezoelectric and pyroelectric properties. However the toxicity of lead oxide and its high vapor pressure during processing have led to demand for alternative lead free piezoelectric material. So BNT with high remnant polarization (P_r) and electromechanical properties is considered to be appropriate candidate to replace lead contained material [11]. The main drawbacks of BNT ceramics are that they are neither easily poled because of their high conductivity nor easily sintered. These problems can overcome by forming solid solution of BNT with other lead free perovskites system like $BaTiO_3$ (BT) and also $K_{0.5}Na_{0.5}NbO_3$ (KNN). BNT-BT system has attracted considerable attention because of the existence of MPB near $x = 0.06$. Composites close to MPB provides improved polling and piezoelectric properties.

2.3 BNT-BT properties by different synthesis method:-

According to many researcher in solid state synthesis route as Ba^{2+} abounds in crystal boundary ceases ion migration and restrains the growing of grain size reduces with increase in BT content. As the depolarization (T_d) and Curie temperature (T_m) decreases with increasing BT concentration the conductivity of BNT- BT decreases in comparison to BNT [12]. In this composition the value of dielectric loss obtained is low but when but when the temperature is increased above T_m , the value of loss increases. It is also reported that with increase in BT content in BNT – BT coercive field (E_c) and remnant polarization (P_r) increases.

M. Cernea et al. reported that the dielectric and piezoelectric properties value of BNT- BT ceramics derived from sol-gel are smaller than those of samples produced by conventional solid state reaction method, due to the grain size and oxygen vacancies that generates dipolar effect. The reduced grain size has influenced the dielectric and piezoelectric properties with substantial decrease of piezoelectric constant (d_{33}).

The densities and grain dimensions of Spark Plasma Sintered ceramics increase with the increasing value of sintering temperature. Permittivity values increases with the increase of sintering temperature. The dispersion of the permittivity and losses are characteristics to relaxor behavior of the ceramics [13].

According to J. Electroceram(2009) 22:203-269 paper BNT-BT ceramics is produced with switching temperature values around 210°C by increasing the $B_{0.5}Na_{0.5}$ contents in ceramics. In Order to to lead content and obtain positive temperature coefficient of resistivity above curie temperature and this property widely used in current control element.

2.4 BNT- KNN Properties by different synthesis method:-

Zuo et al. reported by adding a small amount of (1-x)BNT to xKNN, their structural analysis revealed the coexistence of rhombohedral and tetragonal phase for composition of $x=0.02 - 0.03$ and also piezoelectric coefficient $d_{33}= 196$ pC/N and transition temperature 370° C were reported for this MPB composition[14].

The preparation of KNN-BNT by solid state reaction method shows that the perovskite phase was formed at the temperature as low as 500° C and the average crystalline size of KNN powder tend to change its structure from tetragonal to orthorhombic with increase in crystallite size[15].

2.5 OBJECTIVE

- Synthesize and characterization of high dielectric constant binary ferroelectric materials by microwave processing.
- To study the how the properties varies by synthesizing material by microwave processing.

3. SYNTHESIS PROCESS

3.1 SELECTION OF RAW MATERIAL

For synthesis and characterization process of 12 gms of BNT-BT and BNT-KNN calculated stoichiometric amount of precursors were taken. The precursors used for synthesis of BNT-BT are: Bi_2O_3 , Na_2CO_3 , TiO_2 , BaCO_3 . The precursor amount was calculated by atomic ratio calculation and the respected quantities of precursors are given by $\text{Bi}_2\text{O}_3= 5.8493\text{gm}$, $\text{Na}_2\text{CO}_3 = 1.3044$, $\text{TiO}_2 = 4.2295$, $\text{BaCO}_3 = 0.7312$ were taken. The precursors were taken for the synthesis of BNT- KNN is: Bi_2O_3 , Na_2CO_3 , TiO_2 , K_2CO_3 , Nb_2O_5 . Similarly precursor amount was calculated by atomic ration calculation and $\text{Bi}_2\text{O}_3 = 6.0038$, $\text{Na}_2\text{CO}_3 = 1.4396$, $\text{TiO}_2= 4.0372$, $\text{K}_2\text{CO}_3 = 0.1314$, $\text{Nb}_2\text{O}_5 = 0.5054$ were taken for preparation of BNT – KNN. This much amount of precursor were selected for preparation of sample followed by next step of synthesis.

3.2 BALL MILLING :

Ball milling is a type of grinder specifically used to grind materials into extremely fine powders. It has wide application in various industries such as ceramic and chemical industries.

A conventional ball mill consists of rotating cylinders with appropriate no. of zirconium balls. Zirconium balls are used for ball milling due to its high stability and contamination free properties. The calculated precursors taken for BNT-BT and BNT- KNN were mixed separately then ball milled separately for 20 hrs in acetic medium. After ball milling the sample left for drying and balls are taken out from the powder and the powder is properly grinded with mortar and pestle.

3.3 CALCINATION:-

Calcination is a process of subjecting a substance to heat below the melting point of sample taken, but without fusion, for causing some change in its physical and chemical constituents i.e. removal of water and volatile substance like carbon dioxide . The ball milled powders for BNT-BT and BNT-KNN were taken in two separate crucible and both were calcined at 900°C for 10 minutes in the microwave oven. The condition for calcinations is that the calcinations temperature always less than that of melting temperature of synthesized sample. Greater calcinations temperature gives greater homogeneity of the given sample due to greater extent of heat.

3.4 PALLETIZING

Palletizing is a process of compressing or modifying the material into a particular shape of a palletizer. There are several types of binder used for ceramic pressing but in our synthesis process polyvinyl alcohol is used for binding purpose. First of all the powders were mixed with PVA binder and left for drying for 4 hrs. After drying, the sample grinded into fine powders, then pallets were made with the help of die set and palletizer.

3.5 SINTERING

Sintering is a method of creating objects from powders, including metal and ceramic powder. It is based on atomic diffusion which helps in grain growth. Above absolute zero diffusion occurs in many materials but at higher temperature it occurs faster. The pallets prepared from the raw powder BNT-BT and BNT-KNN were sintered at 1150°C by conventional heating for 3hrs. Sintering is required to densify the pallet and to improve its mechanical strength.

3.5 ELECTRODING:

The electro ding of the sintered pallets can be done by applying silver paste on one of the flat surface. The pallet with silver paste was left for dry upto 6 hrs. Then continuity of those pallets were checked. After checking the continuity the pallets were ready for dielectric measurement.

4 CHARACTERISATION TECHNIQUES

4.1 XRD (X- Ray Diffraction)

XRD diffraction technique is mainly analyzed to to identify components in a sample by a search or match procedure. The crystal structure determination is an indispensable part of characterization of materials, as the physical properties of solids depend on atomic arrangement of material. X- ray diffractometer works on the principle of bragg's law given by

$$2d\sin\theta = n\lambda$$

Where d = spacing between atomic planes

λ = wavelength of X-ray used

θ = angle of diffraction

n = order of diffraction

The accurate determination of lattice parameters provides important characteristics of the materials. In order to measure phase quantity, phase identification, crystallite size determination, quantity measurement (given by peak area) and lattice parameter measurement, calcined powder were characterize. The calcined powder were uniformly mixed then analyzed with X- ray diffractometer with a step size of 0.005. The phase giving maximum peak considered as 100% formation of phase and XRD of that sample also analyzed.

4.2 DENSITY MEASUREMENT:-

The density of the sintered sample can be measured by following Archimedes principle. At first the dry weights of the sintered pallets were measured in weight balance machine. Then the pallets were soaked in glass beaker containing kerosene, after that the beaker containing pallet was kept in desiccator followed by vacuum supply for 6 hrs. Then suspended measurement, by hanging the pallets in kerosene was taken and then pallets were dried using filter paper to remove kerosene and soaked weight measurement was taken by weight balance machine. So the bulk density can be given by

$$\text{Bulk Density} = (\text{Dry weight}) / (\text{soaked weight} - \text{suspended weight})$$

$$\text{Apparent porosity} = (\text{soaked weight} - \text{Dry weight}) / (\text{soaked weight} - \text{suspended weight})$$

4.3 FE-SEM:-

The SEM is a non destructive technique reveals the morphology and composition of synthesized material. The principle of FE-SEM is based on the field emission cathode in the electron gun of scanning electron microscope provides however beam of electrons which when strikes the sample the secondary electrons, X-rays and backscattered electrons are ejected from the sample. These electrons are collected by the detector which gives the information about the sample by converting into signal that displays on screen. Most of the researchers used this technique to get

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

The SEM micrograph was taken on the surface of the sample using scanning electron microscope. Before that the sample were made conducting by coating a thin layer of platinum. Number of lines of known length was drawn on the obtained micrograph for the measurement of grain size.

4.5 DIELECTRIC MEASUREMENT:-

Most ferroelectric material behaves as dielectric material. For application purpose the dielectric constant (ϵ_r) dielectric loss ($\tan \delta$) are important parameters. These dielectric properties give information about the stability of material for application purpose.

First of all the pallets were made conducting by applying silver paste coating for dielectric measurement. Then LCR meter was used to measure relative permittivity (dielectric constant) and dielectric loss at a desired frequency (1 kHz, 10 kHz, 100 kHz, 1 MHz) by temperature range from room temperature to 400°C. The LCR meter interfaced with the computer and the data values of capacitance and D factor was collected as a function of temperature. The dielectric constant can be calculated by the following formula

$$C = (\epsilon_0 * \epsilon_r * A) / d$$

$$\epsilon_r = (\epsilon * d) / (\epsilon_0 * A)$$

Where,

C : Capacitance in farad (F)

ϵ_0 : Permittivity of free space in farad per meter ($8.85 \times 10^{-12} F/m$)

ϵ_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)

By analyzing the dielectric data we can confirm the nature of the material whether it is normal relaxor or normal ferroelectric.

4.6 P-E HYSTERESIS LOOP

The nonzero value of polarization in the absence of applied field is called the spontaneous polarization, which is reversible in case of ferroelectric ceramic. It means the spontaneous polarization can be reversed by applying electric field in the in the opposite direction. A P-E loop tracer gives a plot of polarization versus applied field (E) at a given frequency. The spontaneous polarization, remnant polarization (P_r) and coercive field (E_c) and be measured by hysteresis loop. Hysteresis measurement gives confirmation about the ferroelectric properties of material. Here polarization was studied using the radiant radiant technology i.e. P-E loop tracer by varying the field for two voltages 5000v and 6000v.

5. RESULT AND DISCUSSION

5.1 X- ray diffraction study :-

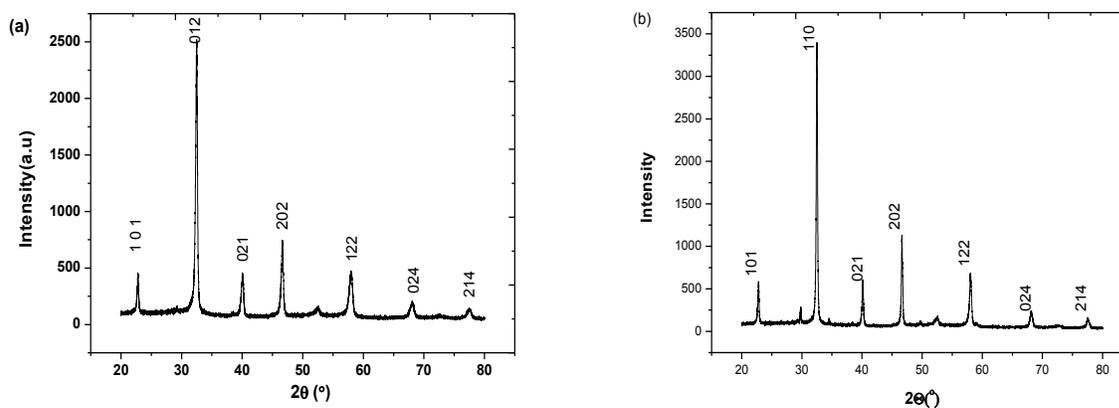


Figure 7. (a) X-ray diffraction pattern of $(0.93\text{Bi}0.5\text{Na}0.5)\text{TiO}_3 - 0.07\text{Ba-TiO}_3$ ceramics and (b) X-ray diffraction pattern of $(0.93\text{Bi}0.5\text{Na}0.5)\text{TiO}_3 - 0.07\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$

Figure 7 (a) shows the X-ray diffraction pattern of $(0.93\text{Bi}0.5\text{Na}0.5)\text{TiO}_3 - 0.07\text{Ba-TiO}_3$ ceramics calcined at 900°C for 10 minute by microwave process. All the composition exhibit a pure

perovskite structure and no second phase is observed; which implies that BT ceramic has diffused into $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ lattices to form solid solution.

Figure 7 (b) shows the XRD pattern of $0.93\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - 0.07\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ Calcined at 900°C for 10 minute processed by microwave. One secondary phase is observed which doesn't matches with BNT phase. This small secondary peak may be due short time duration for the processing of the sample but in can be negligible though all other phases matches with the BNT phase. The XRD patterns are analyzed within the existing pattern in the ICDD data base and the corresponding data for BNT-BT and BNT- KNN are given below in the table.

Sample name	Reference code (ICDD)	Crystal system	Space group and space group number	Lattice parameter a (Å),b (Å), c(Å) and Alpha (°),Beta (°),Gamma (°)	density	volume
BNT-BT	36-0340	rhombohedral	R	5.4760 , 5.4760 , 6.7780 and 90,90,120	5.99	176.02
BNT-KNN	36-0340	rhombohedral	R	5.4760 , 5.4760 , 6.7780 and 90,90,120	5.99	176.02

5.2 Density measurement:

The density measurement of BNT-BT and BNT-KNN is given below in the table

Sample name	Dry weight (in gm)	Suspended weight (in gm)	Soaked weight (in gm)	Bulk density (in gm/cc)	Apparent porosity
BNT-BT	0.3577	0.3082	0.3590	5.70	0.02
BNT-KNN	0.3568	0.3055	0.3584	5.46	0.03

5.3 Dielectric measurement:-

➤ Dielectric constant:-

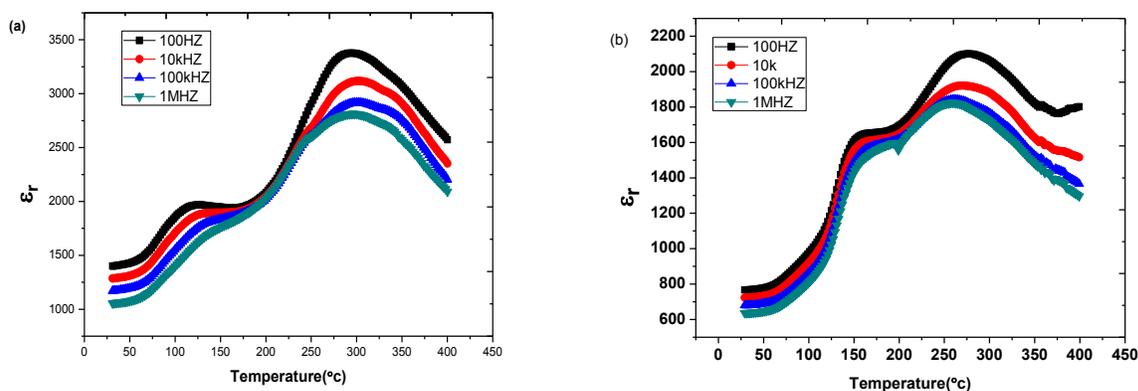


Figure 8 (a) shows plot between dielectric constant and temperature for BNT-BT and (b) shows plot between dielectric constant and temperature for BNT-KNN

The above graph shows the variation of dielectric constant with temperature ranging from room temperature to 400°C with various frequency range 100Hz, 10 kHz, 100 kHz, 1MHz. Figure 2. (a) Is the dielectric constant plot for BNT- BT ceramic shows that dielectric constant decreases with higher frequency? In the above graph we obtained that the dielectric constant of lower frequency i.e. 100Hz gives maximum peak at value of 3369.43 at high temperature 288°C where as the maximum frequency

i.e. 1 MHz gives lowest value of 2800.12 at high temperature temp 286°C . In figure 2 (b) the dielectric constant of lower frequency (100Hz) gives maximum peak at a value of 2097.12 at temperature 271°C but highest frequency gives lowest peak at 1823.99 at temperature 259°C. The dielectric curve here shows two anomalies, one shows first peak shows phase transformation from ferroelectric to antiferroelectric phase and the second peak shows diffusive phase transition from antiferroelectric to paraelectric phase. The nature of graph is same in case of both BNT-BT and BNT-KNN but they have different dielectric constant values at a particular frequency. The nature of graph is same in case of both BNT-BT and BNT-KNN but they have different dielectric constant values at a particular frequency.

Dielectric loss:

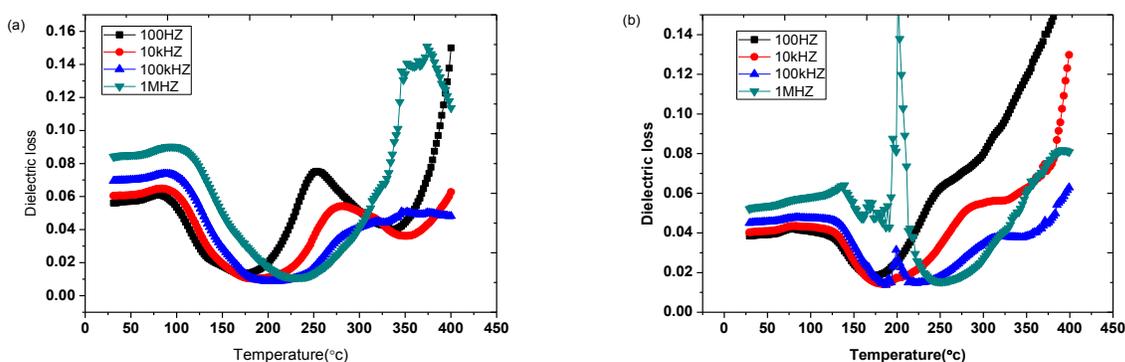


Figure 9 (a) shows graph between dielectric loss and temperature for BNT-BT and (b) shows graph between dielectric loss and temperature for BNT-KNN.

The value of dielectric loss ($\tan\delta$) in the binary composition in both BNT-BT and BNT-KNN is found of the order of 10^{-2} indicating low loss dielectric material. The lowest frequency (100Hz) gives lowest dielectric loss at a value of at room temperature. In plot (a) of the BNT – BT has the dielectric loss value at 0.08 at temperature 34.1 at frequency 1 MHz but at frequency 100Hz dielectric loss value is 0.05 at temperature 34.1°C. In plot (b) BNT-KNN has dielectric loss value 0.05 at temperature 31°C at 1MHz frequency where as in frequency 100Hz dielectric loss value is 0.03 at temperature 31°C. Among these two ceramics BNT-BT shows high loss where as BNT-KNN shows low loss.

➤ Room temperature frequency variation:-

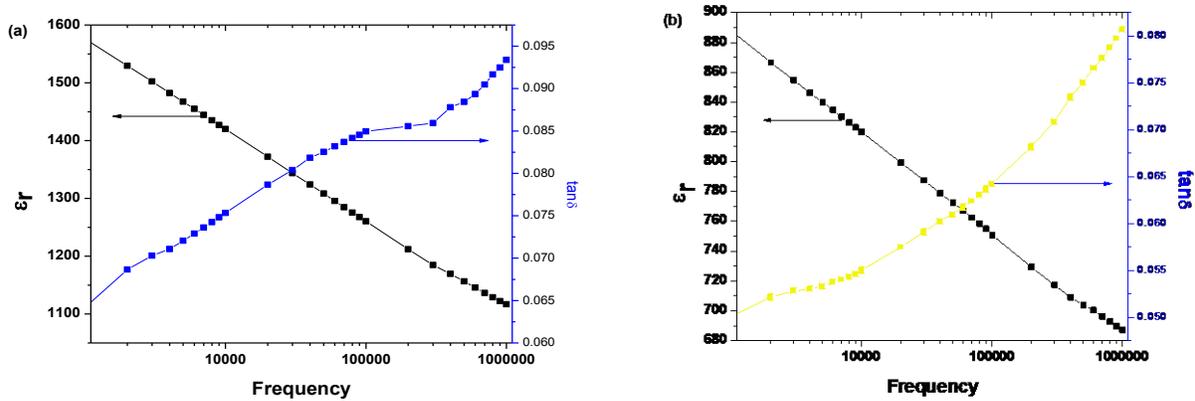


Figure 10 (a) shows the dielectric versus frequency plot for BNT-BT and (b) shows Dielectric versus frequency for BNT-KNN.

The above plot for both BNT-BT and BNT-KNN shows that dielectric constant decreases with increasing frequency but dielectric loss increases with increasing frequency at room temperature. At high frequency there is high dielectric loss which indicates that minimum energy is absorbed at that frequency.

➤ Diffusivity:-

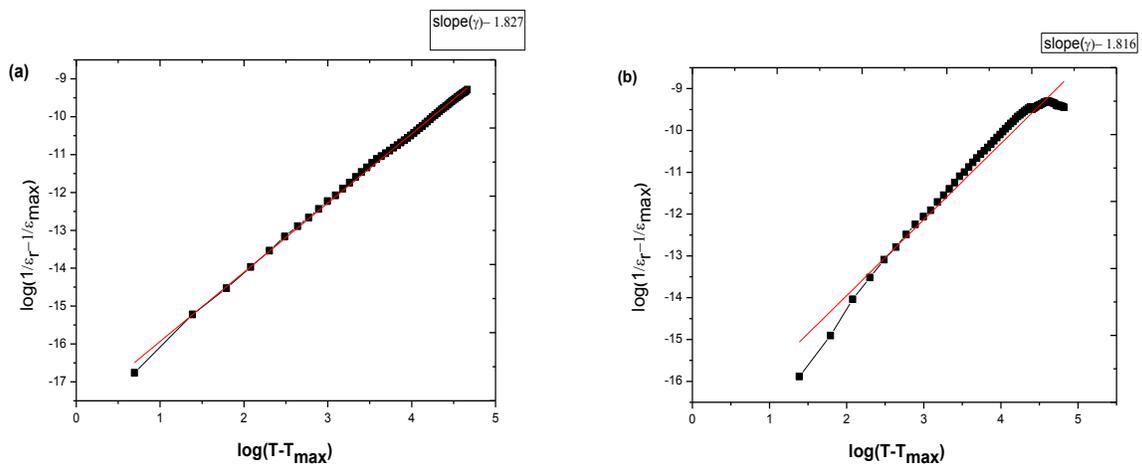


Figure 10 (a) shows graph between $\log(1/\epsilon_r - 1/\epsilon_{max})$ versus $\log(T - T_{max})$ for BNT-BT and (b) shows the graph between $\log(1/\epsilon_r - 1/\epsilon_{max})$ versus $\log(T - T_{max})$ for BNT-KNN

Figure 10 shows the variation of $\log (1/\Sigma_r - 1/\Sigma_{\max})$ with $\log (T - T_{\max})$ from which the nature of phase transition can be determined by calculating the degree of diffusion (γ). The slope of the graph gives the value of γ . From the slope of plot (a) we found γ value to be 1.827 which is nearly equal to 2 and from the slope of plot (b) γ value is found to be 1.816 which is also nearly equal to 2 which in turn suggest that phase transition is diffusive type. The cause of phase transition may be due to structural disorder and compositional fluctuation.

5.4 FE-SEM analysis :-

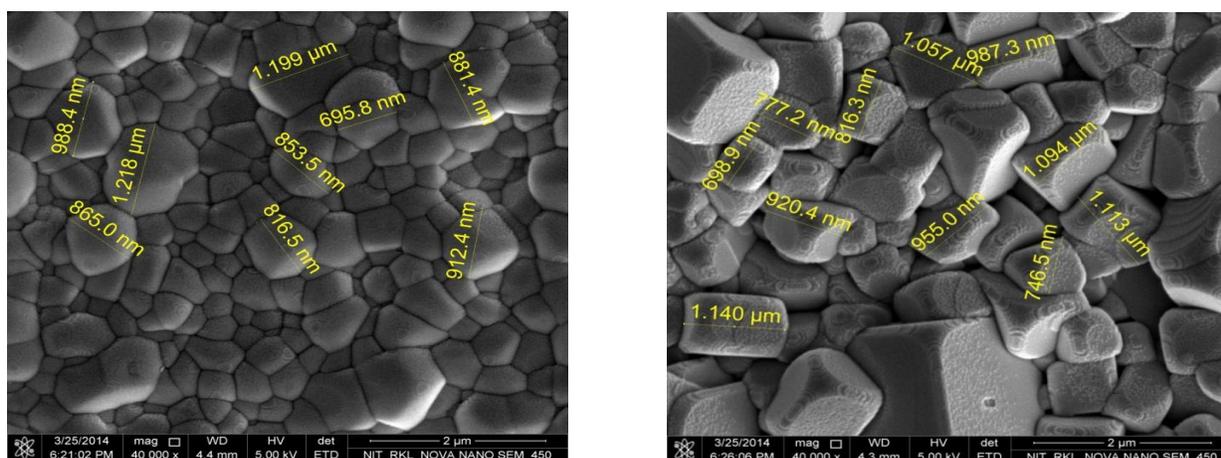


Figure 11 (a) shows SEM micrograph of BNT-BT sintered pellets at 1150°C and (b) shows SEM micrograph of BNT-KNN sintered pellets at 1150°C

In figure 11 (a) SEM micrograph shows the polycrystalline nature of sample having spherical type of grain of different sizes and distributed non-uniformly throughout the sample surface. The calculated average grain size is 936.22. In figure 11 (b) SEM micrograph also shows polycrystalline nature of sample. And it has rectangular type grains non uniformly distributed and of different size. For BNT-KNN and the calculated average grain size is 965.21.

5.5 P-E Hysteresis loop Study:-

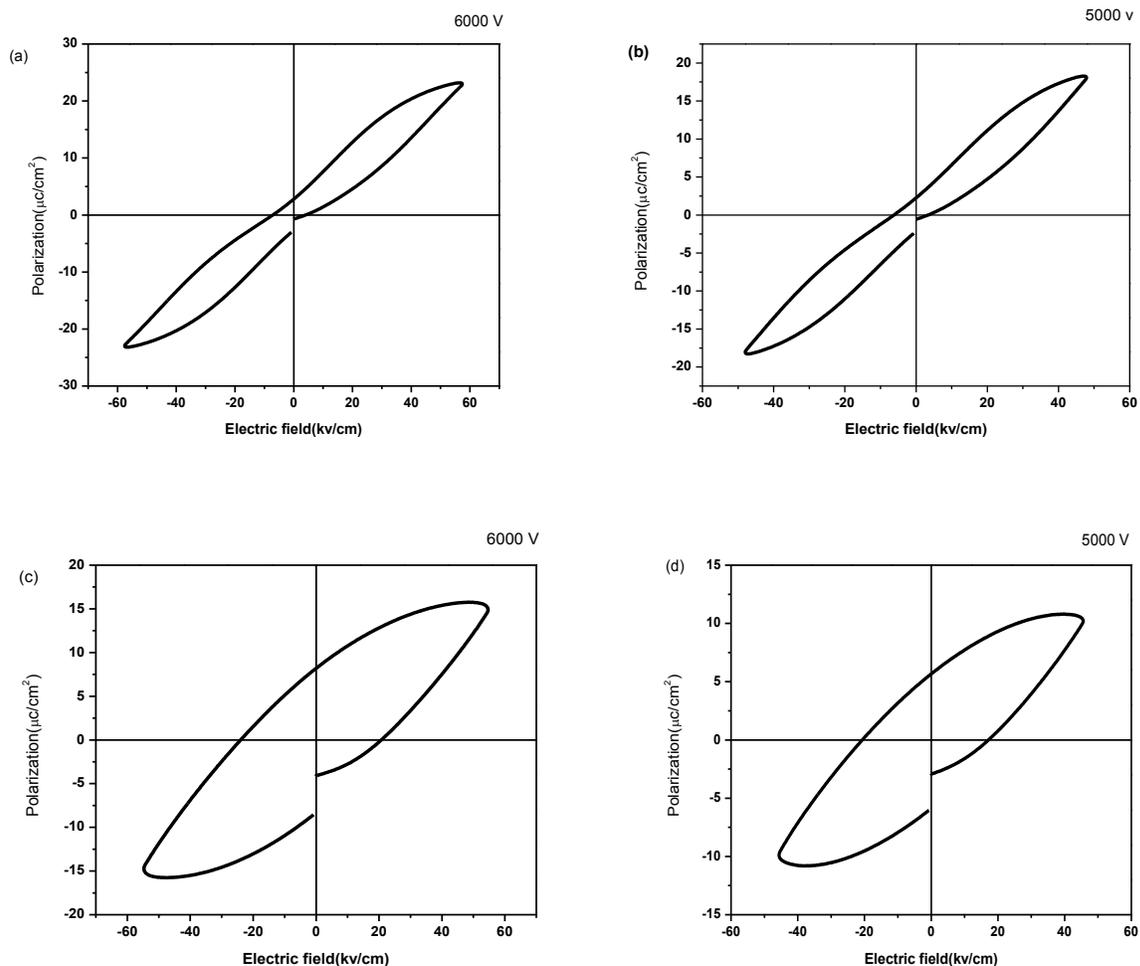


Figure 10 (a) and (b) Shows P-E Hysteresis loop of BNT-BT at 6000 V and 5000 V respectively and figure (c) and (d) shows P-E Hysteresis loop of BNT- KNN at 6000 V and 5000 V respectively.

From P-E hysteresis loop it can be easily seen that in BNT-BT plot (fig (a) and (b)) there is some pinching near the origin which represents the properties of antiferroelectric material but no such pinching is observed in case of BNT- KNN (in figure (c) and (d)) and it shoes ferroelectric properties of material. The remnant polarization, coercive field and saturation polarization value is given in the following table

Sample name	Remnant polarization (in $\mu\text{C}/\text{cm}^2$)	Coercive field (in kV/ cm)	Saturation polarization (in $\mu\text{C}/\text{cm}^2$)

BNT- BT at 6000 V	2.95	6.32	22.90
BNT –BT at 5000 V	5.49	4.49	18
BNT-KNN at 6000 V	7.06	23.86	15.69
BNT- KNN at 5000 V	6.85	23	11

6. CONCLUSION

- 6 By solid state reaction route single phase BNT-BT and BNT-KNN successfully synthesized.
- 7 XRD pattern shows that a pure phase is obtained for BNT-BT by matching the peaks with ICDD data base but a small secondary peak obtained for BNT-KNN which can be neglected though all other peaks matches perfectly.
- 8 SEM images show the polycrystalline nature of the material with no porosity and none uniformly distributed throughout the sample.
- 9 P-E Hysteresis loop shows that among these two binary materials BNT-BT shows antiferroelectric properties where as BNT-KNN shows ferroelectric properties.
- 10 Dielectric studies for both the material shows almost the same characteristics i.e. the dielectric constant and dielectric loss variation with temperature is same in both the cases. Both of the material shows diffusive phase transition.
- 11 By microwave processing prepared sample has given good results by less consumption of time and energy.

7. REFERENCES

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