

CHARACTERIZATIONS OF LEAD FREE BNT-BT-KNN CERAMIC SYNTHESIZED BY MICROWAVE TECHNIQUE

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CERTIFICATE

This is to certify that, the work in the report entitled **“Characterizations of Lead Free BNT-BT-KNN Ceramics Synthesized by Microwave Technique”** by **Miss Anindita Das**, for the partial fulfilment of the requirements for the degree of **MASTER OF SCIENCE IN PHYSICS**, at **NIT, Rourkela**; is a reliable work carried out by her under my supervision and guidance. The work is satisfactory to the best my knowledge.

Dr. Pawan Kumar.

National Institute of Technology, Rourkela

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ABSTRACT

Ferroelectrics have experienced a great deal of interest for more than half a century. Initially, ferroelectric ceramics were used as capacitor materials due to their high dielectric constants. With the preface of lead-zirconate-titanate (PZT), applications spread to transducers, actuators and many others. But because of the toxic nature of lead and serious environmental concerns there is an urgent need to develop lead free ferroelectrics to replace the currently leading lead based PZT. However, recognized lead-free ferroelectrics are not yet good enough to replace lead based materials. A considerable research attempt into lead-free alternatives to PZT began a few years ago. The purpose of this project was to develop lead-free ferroelectrics, which may ultimately replace PZT. The concept of combining three ferroelectric materials, which is before now morphotropic phase boundary compositions, in order to additional increase the ferroelectric properties was studied in detail. The three base compositions chosen were (0.89BNT-0.06BT-0.05KNN) and (0.92BNT-0.06BT-0.02KNN). BNT-BT-KNN was prepared by the solid state route. Calcination of the samples was done by using microwave at 900°C for both 10 and 20 minutes. In both the cases the phase was formed and the 10 minutes calcined samples were chosen for further synthesis to reduce the processing time. XRD of the compositions was done in which a single perovskite phase was formed. The samples were sintered using the microwave sintering method at 1150°C for 30 minutes. FESEM images of the samples were taken which show dense microstructure with uniform grain size and less apparent porosity. The study of dielectric properties and PE loop measurements were done to prove the ferroelectric nature of the sample.

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INTRODUCTION TO DIELECTRICS AND FERROELECTRICS

1.1 DIELECTRICS:

Dielectrics are insulation materials comprise of liquid, gases, and solids. In dielectrics, like the electrons are bound to the molecules and there are no free charges. When these materials are placed within an external electric field, the positive charge centres are moved along the applied field direction while the negative charge centers are displaced in the opposite direction. Therefore dipoles are created in all the atoms within the material. The action of producing electric dipoles which are orient along the external field direction is called dielectric polarization. There are basically four types of polarization. One is atomic polarization where the electrons and nucleus of an atoms are placed w.r.t. each other. Another is ionic polarization arises due to dislocation of a charged ion relative to other ions inside the material. There are furthermore dipole and orientation polarizations where dipoles in the material reorient and the build up of charges at the border or at the grain boundary of polycrystalline material.

On the basis of electromagnetic theory, the total charge on the parallel plate capacitor with dielectric material between the plates is equal to the addition of the surface charge present in a vacuum capacitor ($\epsilon_0 * E$) and additional charge ensuing from polarization of the electric dislocation.

$$D = \epsilon_0 * \epsilon_r * E = (\epsilon_0 * E) + P$$

$$\text{Or } P = \epsilon_0 * E * (\epsilon_r - 1) = \chi_e * \epsilon_0 E$$

Where ϵ_0 is the dielectric constant or permittivity of the free space χ_e is called the dielectric susceptibility and is articulated as $\chi_e = (\epsilon_r - 1) = [P / (\epsilon_0 E)]$. This imply that susceptibility is the ratio of polarised charged to the surface charge in a vacuum capacitor. Where ϵ_r is the relative dielectric constant. [1,2]

1.2 FREQUENCY DEPENDENCE OF DIELECTRIC CONSTANT:

Due to anomalous dispersion, there is drop in the permittivity (ϵ) of the dielectric material with rising frequency of the applied field. The performance of a dielectric material in alternating electric field shows that the dielectric constant which is a complex quantity. The

imaginary part of the constant represents the dielectric loss. It is the dissipation of energy during the movement of charges in an ac field as polarisation switches direction.

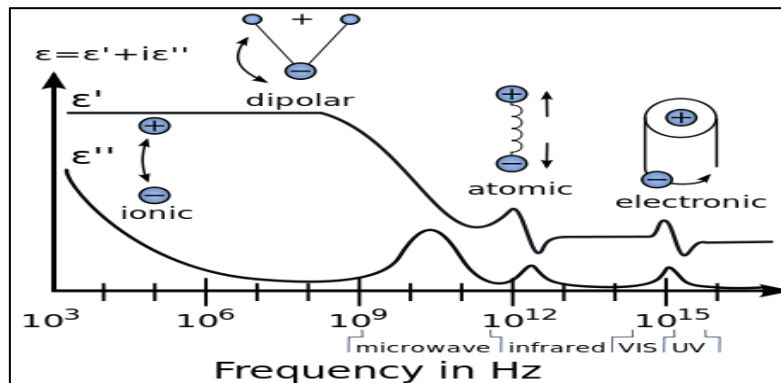


Fig 1: variation of dielectric constant w.r.t. frequency [8]

On the appliance of an alternating electric field (frequency less than 10^6 Hz), there is orientation of electric dipoles within the dielectric material. The polarization follows the field without any delay so that the permittivity remains constant. With the increase in the frequency of the applied electric field from 10^6 Hz to 10^{11} Hz (RF frequency), the polarization lags behind the field and orientational polarization ceases. So the dielectric constant changes, while ionic and electronic polarization present. The action arising during the move from full orientational polarization at zero or low frequency to negligible orientational polarization at rf frequency is referred to as dielectric relaxation

Yet again further increasing the frequency from 10^{11} Hz to 10^{14} Hz (infrared wave frequencies), the positive and negative ions present inside the material cannot follow the field variations, hence the ionic polarization ceases and also changes the dielectric constant value. The electronic polarization exists up to 10^{15} Hz and above this frequency, all polarization ceases.[2]

1.3 FERROELECTRICS:

Ferroelectrics are the dielectric materials and have spontaneous polarization i.e. they have electric dipole moment in the absence of an external electric field. They also hold reversible spontaneous polarization and hysteresis loop behaviour that can be observed in certain temperature region.

1.4 TYPES OF FERROELECTRICS:

On the basis of variation of ϵ_r w.r.t. frequency, the ferroelectrics are classified as normal or relaxer ferroelectrics.

1.4.1 Normal Ferroelectrics:

Normal FE have micro size ferroelectrics domains and has a large remnant polarization. They obey Curie-Wise law and their T_c does not change with frequency. They have well defined P-E hysteresis loop. Normal FE does not show any hysteresis loop at T_c .

1.4.2. Relaxer Ferroelectrics:

They have thin hysteresis loop due to the nano size polar domains. They have second order diffused phase transition. There is strong deviation from the Curie Wise behaviour. It shows a hysteresis loop about T_c . Relaxer Ferroelectric's Curie temperature is not clearly defined. They used as capacitor materials. They have high value of dielectric constant and the capacitance is highest near the Curie temperature. The relaxer FE have a large temperature range than normal FE in capacitive applications.[3]

1.5 PROPERTIES OF FERROELECTRICS

1.5.1 Ferroelectric Crystals:

In crystal symmetry there are 230 crystallographic space groups among which the point groups are only 32. These point groups are again subdivided as shown in the diagram.[4]

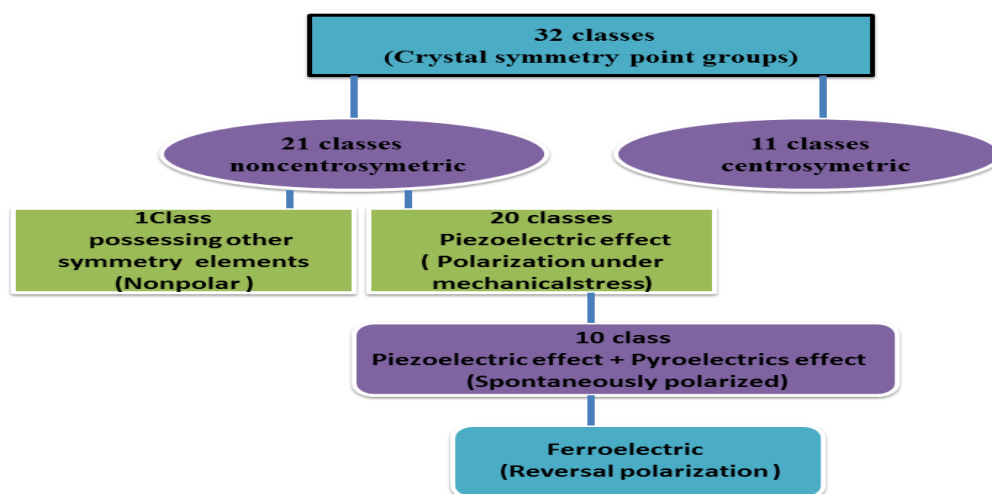


Fig 2: classification of crystal symmetry point groups.

1.5.3 Spontaneous Polarisation and Pyroelectric Effect:

Spontaneous polarization is defined as the dipole moment per unit volume on the surface perpendicular to the axis of spontaneous polarization in the absence of external field. The maximum value of remnant polarization is equal to the spontaneous polarization of a material at a given temperature. The spontaneous polarization is a function of temperature. It decreases with increase in temperature as dipoles are disoriented due to increase in thermal energy. At Curie temperature the spontaneous polarisation vanishes.

In pyroelectric crystals, the displacement is not changed by the electric field of maximum strength. In these crystals to observe a change in spontaneous moment we have to change the temperature i.e. $\Delta P_s = p * \Delta T$

Where p is the pyroelectric coefficient, ΔT is a small change in temperature and ΔP_s is the small change in the spontaneous polarization vector.[4]

1.5.4 P-E Hysteresis Loop for Ferroelectricity:

In ferroelectric materials reversible spontaneous polarization exhibit a hysteresis loop below Curie temperature T_c which is similar to ferromagnetic materials. Above Curie temperature, the electric moments in ferroelectric materials are disorganised, and in the absence of polarisation the ferroelectric material behaves like normal dielectrics materials.

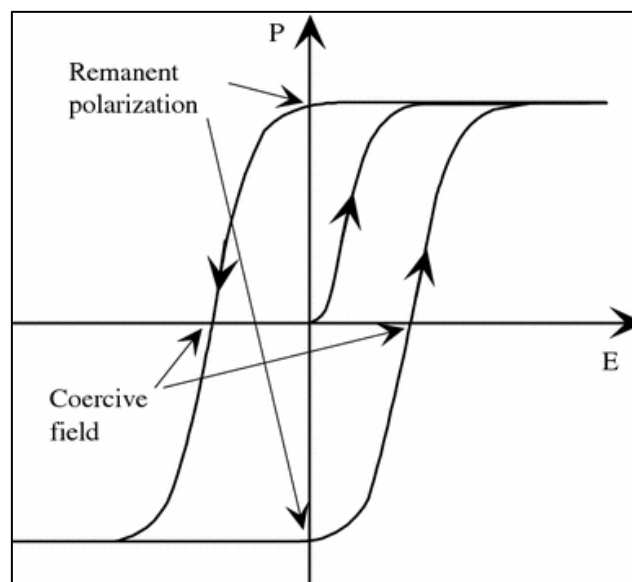


Fig 3: P-E hysteresis loop for ferroelectric materials

The figure shows a hysteresis loop in the electric field vs polarization curve in a ferroelectric material. On the application of electric field along the positive direction, the polarization increases and at saturation all the domains are oriented in one single direction. When the field strength is decreases the direction of polarisation remains unaltered up to a specific reverse field (coercive field). A negative field is required is called coercive field to make the polarisation equal to zero. In ferroelectrics when the external field is removed, the polarization does not drop to zero. In the absence of external field, some of the domains remain aligned in the previously applied field direction. This is why the crystal shows a remnant polarization.[5]

1.5.5 Structure of Ferroelectrics:

Basically the ferroelectric materials were four types. Which are,

1. The corner sharing octahedral
2. Compounds containing hydrogen bonded radicals
3. Organic polymers
4. Ceramic polymer composites

Among these four types of ferroelectric materials the corner sharing octahedral cover a large class of ferroelectric crystal in which perovskite structure compound is one.[6]

The general chemical formula of perovskite is ABO_3 where A and B are two cations of two different size and O is an anion which bonded to both. The size of A atom is outsized than the that of B atoms. Some non-cubic variations like ortho-rhombic and the tetragonal phases also play an important role. Now a day most of the material science experiment is done by using the materials having perovskite structure because, perovskites show many material properties like ferroelectricity, superconductive, charge ordering, spin dependent transport etc.

The material like Bariumtitanate ($BaTiO_3$), Bismuthsodiumtitanate (BNT), Potassiumsodium niobate($K_xNa_{1-x}NbO_3$), Leadzirconate titanate (PZT) etc. have perovskite structure and also show the FE as well as piezoelectric properties.

Consider the order of magnitude of the ferroelectric effect in BT, below Curie temperature the structure of BT is slightly deformed with Ba^{2+} and Ti^{4+} ions displaced relative to the O^{2-} ions, there by developing a dipole moment. The observed saturation polarization P_s at room temperature is 8×10^4 esu cm^{-2} . [7]

1.5.6 Ferroelectric Phase Transition:

The polarisation of a ferroelectric or anti ferroelectric exists up to the Curie temperature. There is a phase transition from EF or AFE to Paraelectric phase take place at Curie temperature. Kittle well-defined the antiferroelectric states in which lines of ions in the crystal spontaneously polarised but with adjacent lines polarised in antiparallel direction.

The dielectric properties of the material show an anomalous behaviour at Curie temperature. The temperature dependence of the dielectric constant in ferroelectric is governed by Curie Wisers law at temperature $T > T_c$.

$$\text{i.e. } \epsilon_0 = \epsilon_r + C/(T-T_0)$$

Where ϵ_0 , ϵ_r , T_0 and C are the permittivity, relative permittivity Curie temperature and Curie constant of the material respectively.

Above the temperature 120°C , BT possesses a cubic structure and having a no spontaneous dipole. As it has no dipole, the material behaves like a simple dielectric, giving a linear polarisation. So 120°C is the Curie temperature for BT. Below Curie temperature it changes to tetragonal phase due to the movement of Ti atoms inside O_6 octahedral and it is responsible for the dipole moment. BT has two other phase transitions on cooling further and each phase enhance the dipole moment. The orthorhombic phase is reached when BT is cooled below 0°C .

All the above ferroelectric phase of BaTiO_3 has a spontaneous polarization based on the movement of the Ti atoms in the O_6 octahedral and the Para electric cubic phase is assumed to be their parent phase.

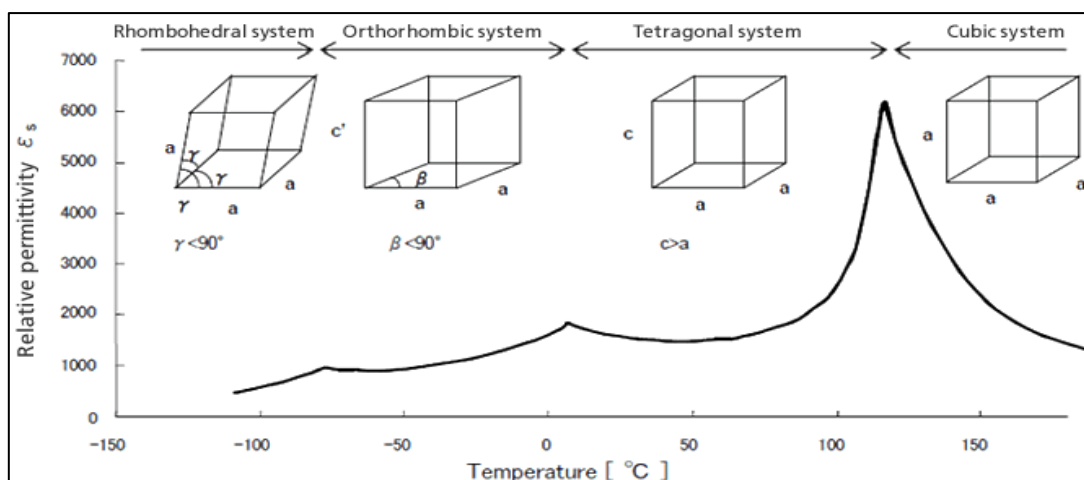


Fig 4: variation of dielectric constant w.r.t. temperature

The sequence of phase transition is Cubic—tetragonal —orthorhombic — rhombohedral.

Near Curie temperature, the spontaneous polarization occurs and domains are generated, with 1% axial elongation in the direction of the C-axis. Domains are regions of uniform polarisation within a FE crystal.

Over a period of time after the generation of spontaneous polarization, they are arranged in a stable state by forming domains. In this state, a higher electric field is required to reverse the spontaneous polarization of domains.

Since the dielectric constant is equivalent to the reversal of spontaneous polarisation per unit volume, if the number of domains with low field reversal is reduced, the capacitance decreases.[10,11]

2. LITERATURE REVIEW

2.1 ADVANTAGES OF MICROWAVE PROCESSING:

Now a day many researchers have reported on the non-thermal phenomena known as “microwave effect”. Such type of effect involves enhanced reaction rates of thermosetting resins during microwave curing and quicker densification rates in ceramic sintering process. In order to optimise the processing phase and temperature it is necessary to understand the microwave / material interaction and material transformations. Wei et al. [12] has investigated the microwave heating in single mode cavities and Thostenson [13] has experimentally studied the microwave heating in a huge multimode opening of thick-section composite. In single mode cavity there is one 'hot spot' where the microwave field strength is high. This is widely used for joint of ceramics. Microwave energy is concentrated at the joint boundary and localised heating of ceramic joint will be achieved. It has size limitation. But multimode applicators are proficient of sustaining a number of higher order modes at a time. The number of possible resonant modes increases with the range of the microwave cavity. Again due to microwave material communication, energy is transferred to materials by interaction of the electromagnetic fields at the molecular level and the effect of electromagnetic field on the material is determined by the dielectric properties.

Halil et.al.[14]used a microwave(microwave) assisted way for the solid state synthesis of lead pyrophosphate ($\text{Pb}_2\text{P}_2\text{O}_7$). In this work they have study a new procedure based on microwave heating which is much faster, cleaner and economical than conventional

techniques. The $\text{Pb}_2\text{P}_2\text{O}_7$ was synthesised and the reaction was ended p in 10 minute. Comparing to the conventional methods, $\text{Pb}_2\text{P}_2\text{O}_7$ was obtained with reduced processing duration, high heating rates and low reaction temperature.

2.2 REASONS FOR SELECTION OF BNT-BT-KNN:

Zhang et al. [15] studied the superstructure of lead free piezoelectric ceramics (BNT-BT-KNN). Lead containing ferroelectric materials, such as $\text{Pb}(\text{ZrTi})\text{O}_3$, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 in either ceramic or crystal form, are currently used in industry. But due to toxicity of lead and high vapour pressure during processing alternative lead free materials are highly advantageous. Rodel et.al. [16] showed that the ferroelectric and electrostrictive performance of BNBT can be improved by adding several percentage of KNN. $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ is an outstanding material of lead free piezoelectric ceramic and has low temperature phase transition $T_d=200^\circ\text{C}$ from ferroelectric to antiferroelectric phase. Barium titanate (BaTiO_3) has a rhombohedral symmetry with tetragonal perovskite structure. The solid solution of BNT with BT leads to a MPB with most pronounced piezoelectric response for the MPB composition $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$. It has orthorhombic structure. Further studied showed that the BNBT with an additional 1-3% of morphotropic KNN gives best response towards various piezoelectric properties like curie temperature ($T_c=250^\circ\text{C}$), FE to AFE transition temperature ($T_d=150^\circ\text{C}$) [16] etc. Again the maximum strain value i.e. 0.45% is obtained which is higher than strains ever reached in other lead free polycrystalline, ferroelectric ceramics. Also maximum value of $S_{\text{max}}/E_{\text{max}}$ ($=560\text{pm/V}$) is obtained [17].

Regarding the MPB compositions, comparable results were reported by Shan-Tao et.al.[18] Phase diagram of BNT-BT-KNN ternary structure has been analysed and pseudocubic structures were confirmed by X-Ray diffraction study. The ceramics $(0.94-x)\text{BNT}-0.06\text{BT}-x\text{KNN}$ ($0.15 \leq x \leq 0.30$) has been prepared. The compositions with $x=0.02$ and 0.25 show the diffused phase transition with pure electrostrictive characteristics and low dissipated energy i.e. the area of the PE loop. In relaxor ferroelectrics, the electrostrictive strain can be kept at a relatively high level in a wide temperature range due to diffused phase transition. The electrostrictive outcome can be very large at room temperature, if the phase transition temperature is close to room temperature. Therefore the compositions or dopant in lead free relaxor ferroelectrics were adjusted to produce pseudocubic/cubic structure at room temperature, which might produce good lead free electrostrictors.

2.3 OBJECTIVE OF THE WORK:

Now days due to the toxic nature of lead, the lead free materials have dominated applications over lead based materials. Again the KNN family presently shows superior properties than that of the other lead free systems. Like PZT system, in KNN system three morphotropic phase boundaries (MPB) exist. By varying the KNN percentage in lead free BNT-BT composition we can enhance the piezoelectric as well as ferroelectric properties.

To understand the goalmouth of this project work, the specific objectives were set as follows:

- To improve the ceramic synthesis route by using MW processing as it saves time i.e. low cycle time and hence the energy.
- To synthesize and characterise the lead-free ferroelectric BNT-BT-KNN ternary system with MW sintering.

3 EXPERIMENTAL WORK AND TECHNIQUES

The ferroelectric material BNT-BT-KNN with two different compositions was prepared using solid state synthesis route and microwave heating mechanism. The synthesis and the characterisation of the samples 0.89BNT-0.06BT-xKNN 0.05 and 0.92BNT-0.06BT-0.02KNN were associated various steps which are described below in details.

3.1 SOLID STATE SYNTHESIS ROUTE:

The solid state route is one of the conventional method for the synthesis of ceramics. Solid state reactions may have the following advantages over other reaction techniques. It is a cheapest route with limited formation of side products. No solvents are needed for the reaction and hence no waste disposal issues. These reactions are often faster, taking just a few minutes rather than hours to complete because the reactants are in close contact with each other. The steps of solid state synthesis are represented in a flow chart.

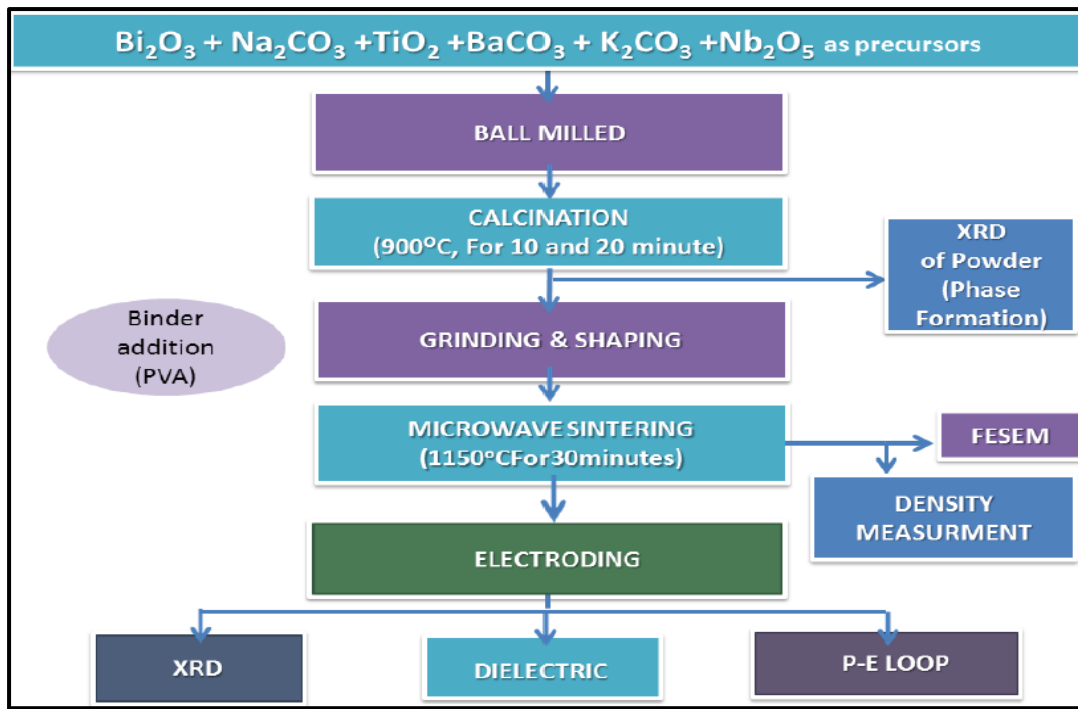


Fig 5: Flow chart for solid state synthesis route.

3.1.1 Selection of raw materials and Stoichiometric Weighing:

The precursors used for the preparation of the BNT-BT-KNN with two compositions were Bismuth oxide (Bi_2O_3), Sodium carbonate (Na_2CO_3), Titanium dioxide (TiO_2), Barium carbonate (BaCO_3), Potassium carbonate (K_2CO_3), Niobium pentoxide (Nb_2O_5) and the amount of precursor was calculated by atomic ratio calculation. After taking the precursor they are weighted according to the calculated stoichiometry because the stoichiometry of the compositions plays an important role in determination of FE ceramic properties.

3.1.2 Mixing:

Mixing can be done by mechanical method. In mechanical mixing a ball mill is used to grind materials in extremely fine powders. After weighing the precursors were ball milled in acetone medium using zirconia balls as grinding medium for complete mixing purpose for 20 hrs. Due to high refractiveness and contamination free nature the zirconia balls are used as grinding media.

3.1.3 Calcination:

During calcination the mixed raw materials are heated at a temperature below its melting or fusing point. Causing loss of moisture, volatile components etc. It also associated with reduction and thermal decompositions or phase transition. The two compositions of BNT-BT-

KNN were taken in two different crucibles for calcination at 900°C with two varying time periods 10minute and 20minute. Due to the solid phase reaction the mixture transformed into a ferroelectric phase. Proper calcination with suitable temperature gives a ceramic product having good density and electromechanical properties.

3.1.4 Grinding and Shaping:

Grinding is necessary for the lumpy calcined product to make it fine powder. Then required amount of polyvinyl alcohol is added to the calcined powder to bind the particle together. Typically PVA is used as a binder because it is stable and does not form and has strong surfactant with high binding power. Palletising is performed after that. This process is associated with compressing a material in to the shape of a pallet.

3.1.5 Sintering:

Densification occurs during sintering. In this process the green body is heated to to a temperature below its melting point until its particles adhere to each other. Initially at low temperature range (500-600°C) the binder borne out stage takes place. After binder borne out sintering takes place in which the ceramic particles are fuse together. Therefore proper sintering is required for the density and electrical measurements.

Both the samples were sintered at 1150°C using MW heating mechanism. MW sintering involves internal volumetric heating of the sample and there is energy conversion takes place. It is a noncontact heating method where heat flows from inside to outside. The MW sintering process has significant advantage over conventional sintering process. MW heating enhances diffusion process, reduces energy consumption, gives very rapid heating rates, and decreases the sintering temperature and processing time.

3.1.6 Density measurement:

Dry weight of all sintered sample were taken and then put the samples in beakers. All the beakers were three fourth filled with kerosene. The beakers were placed inside a vacuum chamber for 30 minute. After vacuum treatment, the suspended weight of each sample was taken and noted down. Finally the soaked weight of the samples were measured. By using the formula: $[D / (W-I)] \times \text{density of the liquid}$ and $[(W-D)/(W-I)]$; where D, W, I are the dry weight, shocked weight and suspended weight respectively the bulk density and apparent porosity can be measured respectively .

Table A: Measurement of bulk density and apparent porosity

Sample name:	Dry weight. (in gram)	Suspended weight (in gram)	Soaked Weight (in gram)	Bulk Density (in g/cc)	Apparent Porosity
0.89BNT-0.06BT-0.05KNN	0.3626	0.3107	0.3635	5.56	0.01
0.92BNT-0.06BT-0.02KNN	0.3662	0.3128	0.3678	5.39	0.02

3.1.7 Electroding:

The sample surface were polished before electroding and then silver past is used the coat of the both side of the pallets surface for electroding. The pallet is now in between tow electrodes like dielectric materials in between parallel plate capacitor. The silver paint should have zero resistivity and good chemical and physical stability. The coating layer should be thin and adhere the sample surface perfectly.

3.2 X-RAY DIFFRACTION:

X-ray diffraction technique is a non-contact sample analysis technique and gives information of crystal structure, chemical compositions, and other physical properties of the materials. It is based on the principle that when X-rays are scattered from a crystalline solid, the scattered radiations can constructively interfere to produce a diffracted beam. The peak of scattered intensity which is observed must satisfy the conditions i.e. the angle of incidence equal to the angle of scattering and the path difference is an integral multiple of wavelengths. The condition for maximum intensity must satisfy the Bragg's law i.e. $2d \sin\theta = n\lambda$ and gives us detail information about crystal structure. In this characterisation method the powder sample is placed in a holder and it is illuminated with X-ray of CuK_α radiation and the intensity of the reflected radiation is recorded using a goniometer. The prepared ceramic samples XRD were done using CuK_α (wave length, $\lambda = 0.15405\text{nm}$) radiation.

3.3 FIELD EMISSION SCANNING ELECTRON MICROSCOPE:

An electron microscope is a type of microscope has greater resolving power than optical microscope. It has a beam of electrons to illuminate the sample. FESEM gives greater resolution and magnification because the wavelength of electron (i.e. de Broglie wave

length), is much smaller than that of a photon of visible light. This technique is used to study the surface topography, morphology, compositions and crystallographic information of the specimen. A beam of electron after generation from a source is accelerated through a high vacuum, a system of apertures and electromagnetic lenses and finally strikes the specimen surface. The kinetic energy of the accelerated electron is dissipated as a variety of signals due to the electron and sample interactions. The various signals which are generated from the interaction volume of the specimen are X-rays, secondary electrons (SE), back scattered electrons (BSE), phonons, Auger electrons etc. The SE and BSE are commonly used for the imaging. FESEM produces an image in a raster scan pattern. In this work, the microstructures of prepared ceramic samples were viewed by using NOVA NANO SEM 450 scanning electron microscope.



Fig 6: Image of Nova nanoSEM

3.4 DIELECTRIC MEASUREMENTS:

The LCR meter is used to study the variation of dielectric constant of the ferroelectric ceramics w.r.t. frequency and temperature. It is basically an inductance (L), capacitance (C) and resistance (R) measuring device. The quantities are determined from the impedance of the sample. The measurements of the electrical properties at low frequencies are based on auto balancing bridge method and for high frequencies employ the RF I-V method. In this technique the device under test (DUT) is placed in bridge. The meter detects the voltage over

and the current through the DUT using Ohm's law and also the impedance. Measurements were made by HIOKI 3532-50 LCR-HITESTER.

3.5 P-E LOOP:

In this project work the PE loop observations were made by using a Sawyer-Tower circuit where the voltage is cycled by the signal generator and its direction is reversed depending on the frequency and then measured the voltage across the reference capacitor. The charge on the ferroelectric capacitor and reference capacitor must be same because of their series connection. So the charge on the ferroelectric capacitor can be measured by using the relation $Q=C/V$ and the polarisation by $P=Q/A$, where C is the capacitance of the reference capacitor, V is the voltage of this capacitor and A is the area of the plates. As the capacitance of the reference capacitor is greater than that of the ferroelectric sample, maximum percentage of the voltage lies on the ferroelectric itself. The polarization in the oscillating field can be plotted by taking the voltage applied to the material along X-axis and the surface charge along Y-axis. The measurement of P is possible by cycling the polarisation through cycling the voltage crosswise the ferroelectric capacitor.

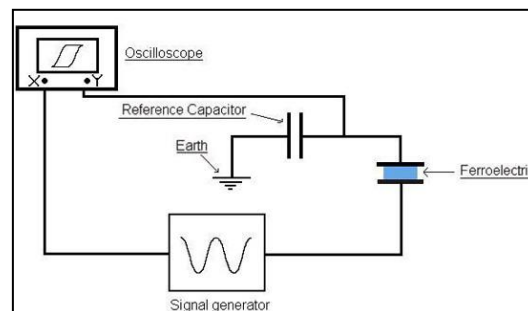
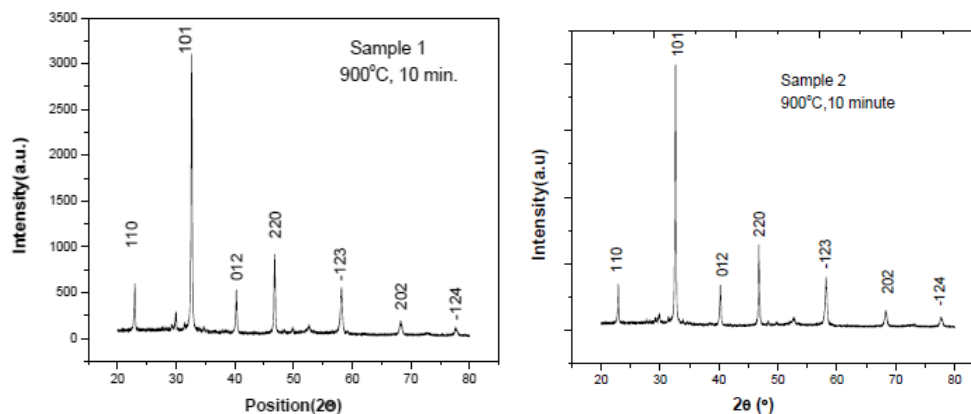


Fig 7: Sawyer-Tower circuit for P-E loop measurement [9]

5 RESULTS ANALYSIS

5.1 X-RAY DIFFRACTION STUDIES:



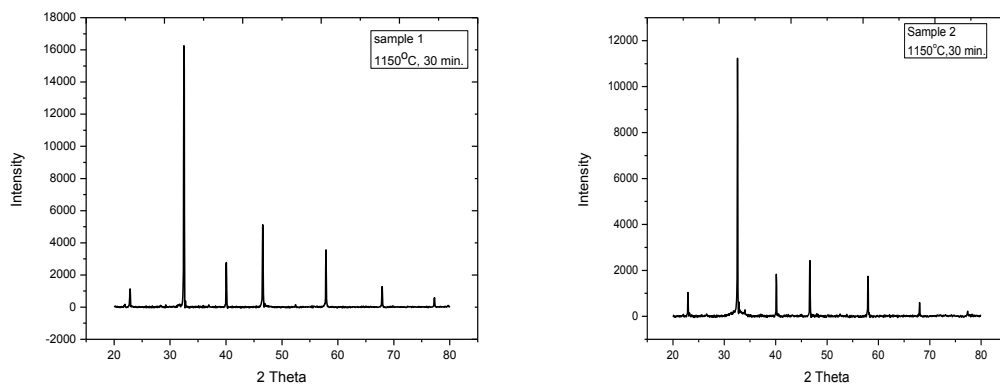


Fig 8: XRD plots of both calcined and sintered samples.

Above figures shows the XRD plots of both the samples calcined at 900^oc for 10 minutes and sintered at 1150^oc for 30 min. by microwave heating method. Both the compositions show a pure perovskite structure, which shows that the precursors are diffused to form solid solutions of BNT-BT-KNN. Some secondary peaks are also present in the graphs which are undetermined.

5.2 FIELD EMISSION SCANNING ELECTRON MICROSCOPE:

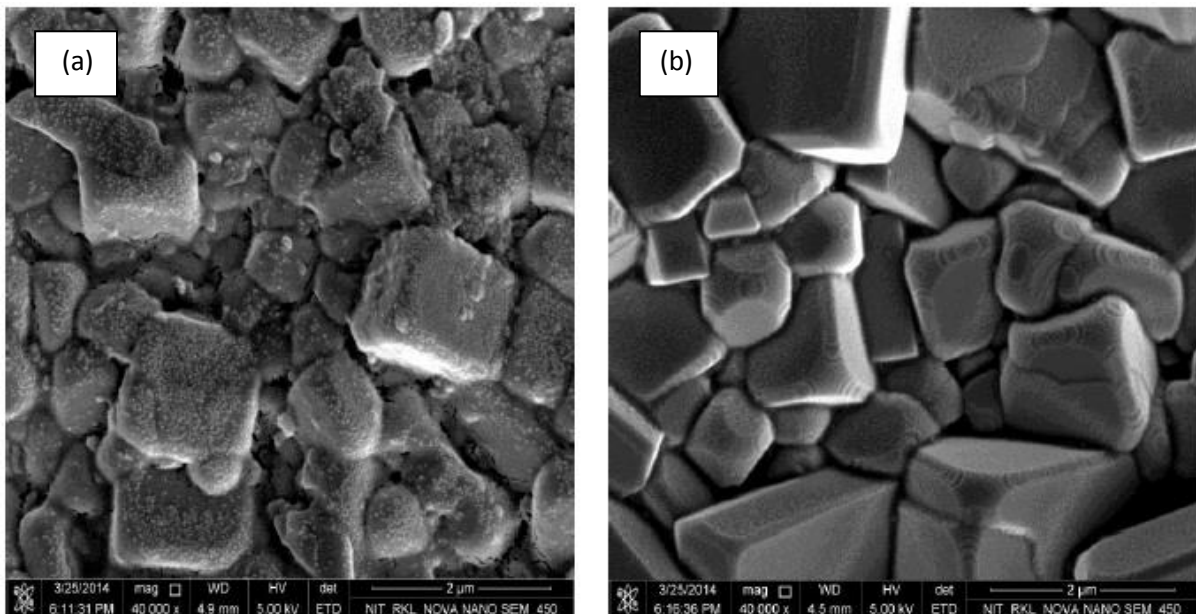


Fig 9: (a), (b) shows the FESEM images of sample 1 and 2.

The surface morphology studies and the images of the micro structures of the sintered ceramic pellets of BNT-BT-KNN were carried out using FESEM are shown in fig 9. The pellets were gold coated for three minutes and scanned under SEM using field emission gun. The (a) and (b) are the FESEM images of sample 1 and 2 sintered at 1150oc for 30 minute. It

can be seen that the samples consist of polycrystalline microstructures with regular brick like quadrangular grains.

5.3 DIELECTRIC MEASUREMENTS:

5.3.1 Variant of dielectric properties with temperature:

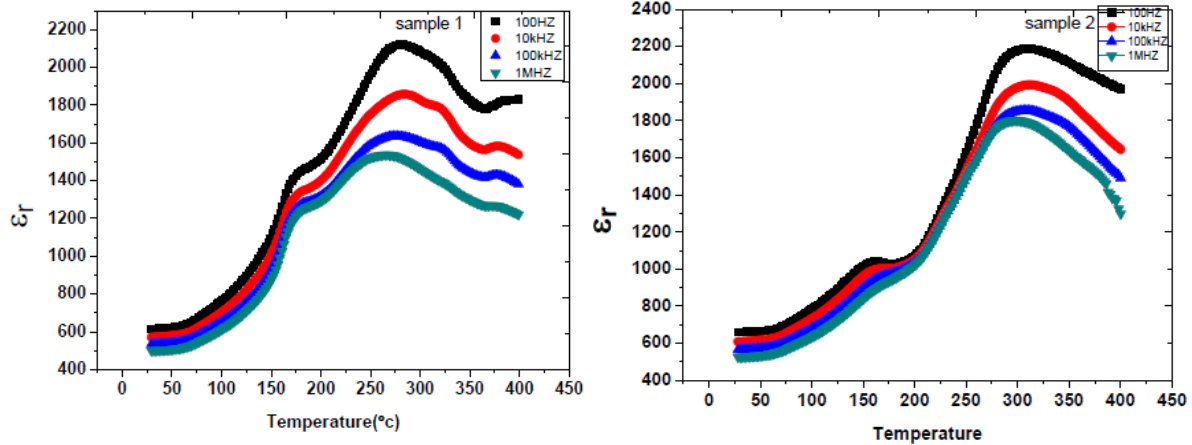


Fig 10: Plots of dielectric constant with temperature.

Temperature dependence of ϵ_r and loss ($\tan\delta$) at a range of variable frequencies ranging from 100 Hz to 1 MHz are shown in the above Fig 10. Different MPB compositions of KNN system are undergoing two phase transitions, first one $\sim 200^\circ\text{C}$ and second one $\sim 400^\circ\text{C}$. It is observed that value of ϵ_r increases with the increase of temperature and shows anomalous behaviour near the phase transition temperatures (T_c). Starting from room temperature to 400°C the dielectric constant attains a maximum value for the minimum value of frequency 100 Hz. From the above measurements we get that sample 1 having 5% KNN has maximum dielectric constant value 2120 and sample with 2% KNN has value 2184.

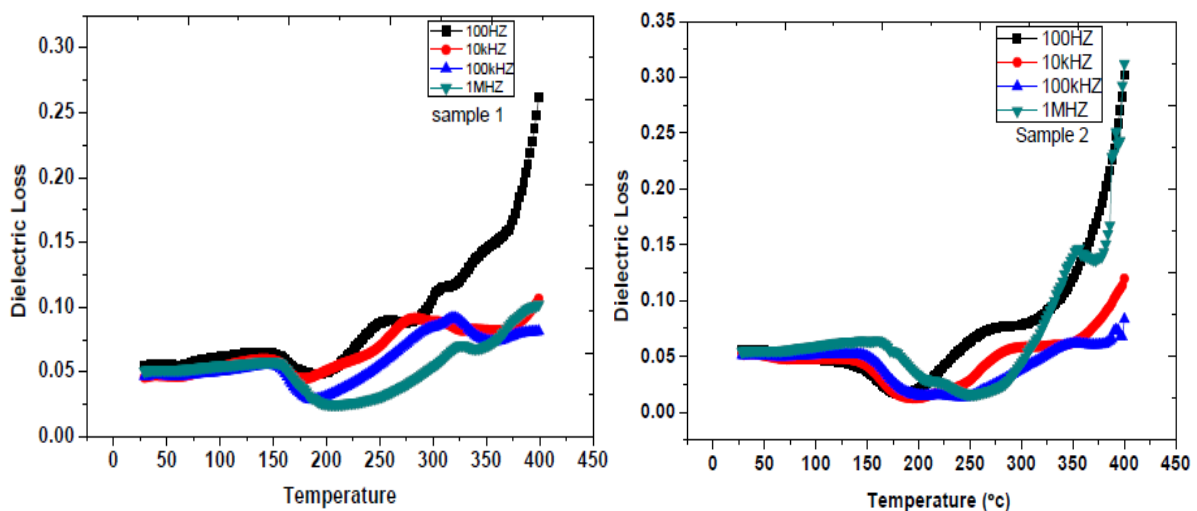


Fig 11: Plots of variation of dielectric loss w.r.t. temperature.

From the graphs the value of dielectric loss ($\tan\delta$) in these ternary compositions is found to be the order of 10^{-2} showing the low loss materials. The composition shows a particular value of dielectric loss i.e. 0.05 for all the frequencies at room temperature.

5.3.2 Degree of diffusion:

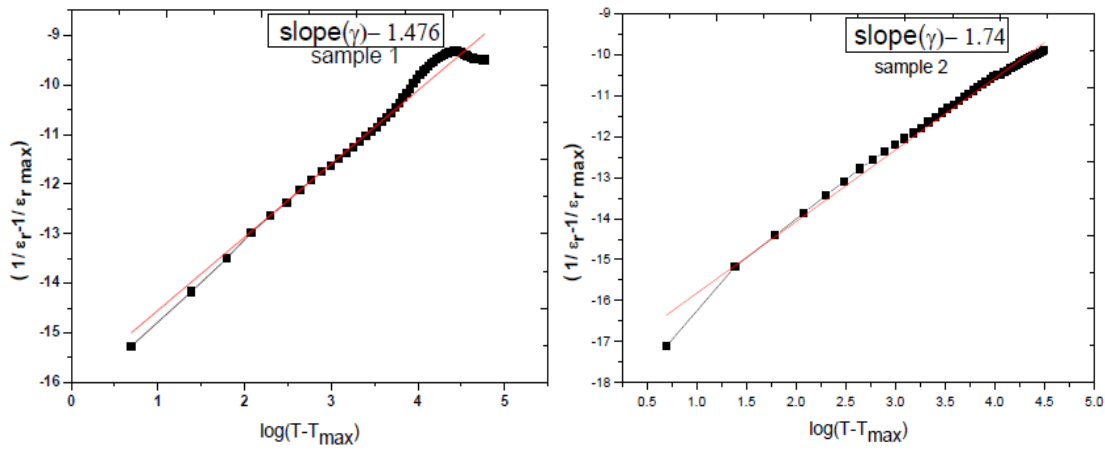


Fig 12: Graphs representing the degree of diffusion of phase transition.

The dielectric studies as function of temperature within the range (room temperature to 400°C) at variable frequencies show that the ceramics go through a phase transition of diffuse type. The slope of the plot between $(1/\epsilon_r - 1/\epsilon_{r\text{max}})$ vs $\log(T-T_{\text{max}})$ gives the degree of diffusion (γ) from which we can collect the information about the nature of phase transition. From the figure (12) and (13) the degree of diffusion is found to be 1.476 and 1.74 for the sample 1 and 2. In both compositions the value of degree of diffusion is nearer to 2 which suggest that the phase transition is a second order diffused type which may arise due to structural disorderness and compositional fluctuation in solid solutions.

5.3.3 Variation of dielectric properties w.r.t. frequency at room temperature:

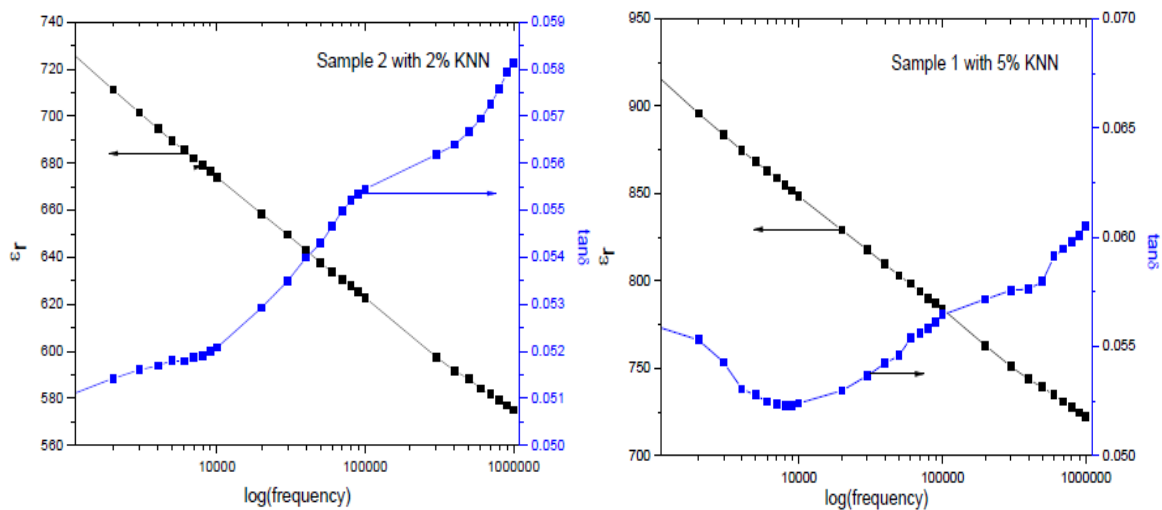


Fig 13: Plots for variation of dielectric properties w.r.t. frequency at room temperature

The Frequency dependence of ϵ_r and dielectric loss ($\tan\delta$) at room temperature of different composition of BNT-BT-KNN system are shown in figure 14. When a dielectric is placed in an ac electric field, the displacement of charges, and the direction of the dipoles are try to follow the direction of applied electric field. But the switching of the orientation of polarisation with the reversal of electric field is much more difficult at high frequencies. Therefore at high frequencies only electronic polarisation exists. In both the graphs the dielectric constant shows an accepted decrease with increasing frequency. The plot dielectric loss vs frequency shows that the loss is maximum at higher frequencies. Basically the resonance frequency at which internal frequencies of the dipoles matches with the external ac electric field frequency is responsible for the maximum loss in dielectric materials.

5.4 PE loop measurements:

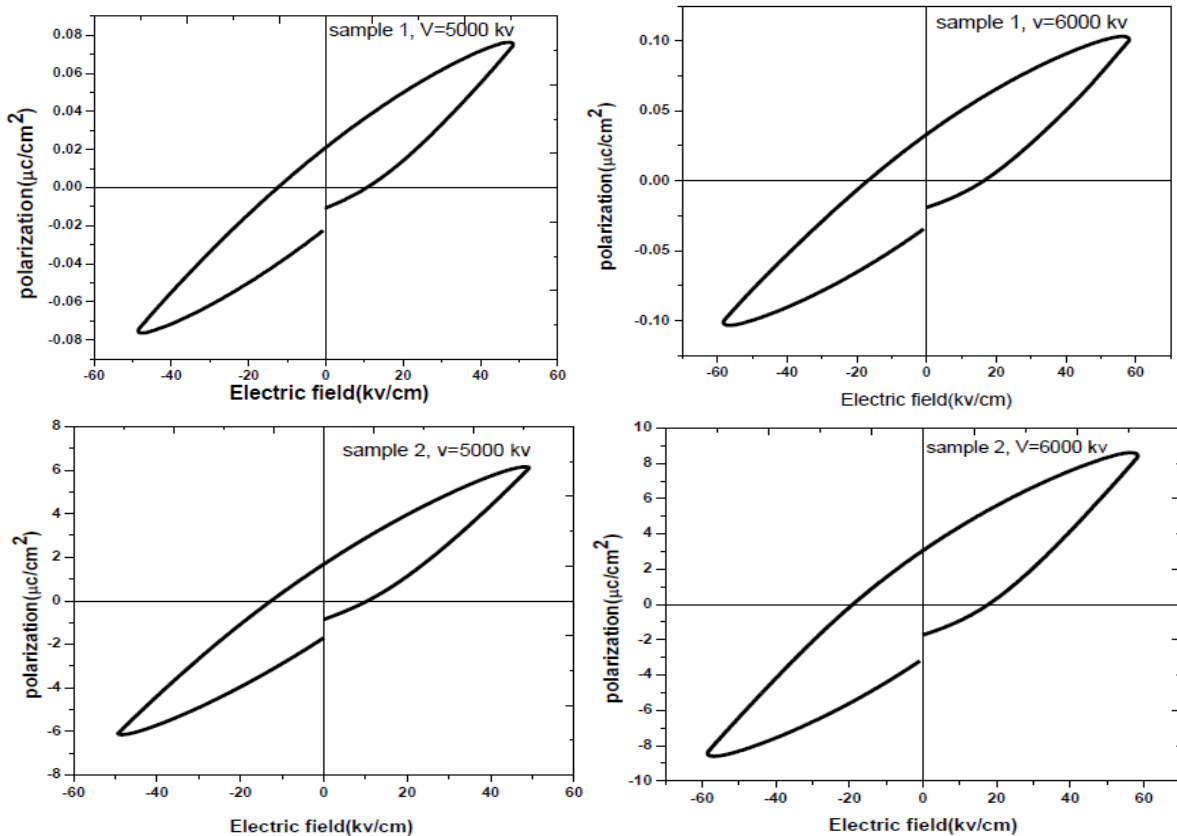


Fig 14: P-E loop measurement of both the samples at two variable voltages.

PE loop of the ceramics were obtain using a conventional Sawyer-Tower circuit. The non-linear nature of the P-E loops confirmed the ferroelectric nature of BNT-BT-KNN. The measured value of remnant polarisation (P_r), coercive field (E_c) and saturation polarisation (P_s) are given in the tables below.

Table .B (For the voltage V=5000 Kv)

Sample name.	Remnant Polarisation (Pr)	Coercive field (Ec)	Saturation Polarisation(Ps)
0.89BNT-0.06BT-0.05KNN	0.02	11.91	0.07
0.92BNT-0.06BT-0.02KNN	1.74	12.94	6.12

Table .C (For the voltage V=6000 Kv)

Sample name.	Remnant Polarisation (Pr)	Coercive field (Ec)	Saturation Polarisation(Ps)
0.89BNT-0.06BT-0.05KNN	0.03	16.43	0.10
0.92BNT-0.06BT-0.02KNN	0.04	18.68	8.54

6 CONCLUSIONS

The mainstream of presently used high performance ferroelectric materials contains lead oxide. But suitable to the biological and environmental concern the scientific society is interested in alternative lead free materials with better performance and large operating temperature ranges for electromechanical transducer application. Microwave sintering yield dense and single phase lead free BNT-BT-KNN samples with variable compositions. Microwave sintering has advantages of low processing time, lower environmental impact and many more. The sintered samples have lesser grain size due to high densification. Dielectric constant obtained in both the compositions is also high. XRD patterns of both the samples yielded monoclinic structure (JCPDS Card No: 46-0001) and single perovskite phase. The P-E hysteresis loop of BNT-BT-KNN was measured which shows the well behaved hysteresis loop, confirm the ferroelectric nature of the BNT-BT-KNN.

REFERENCES

1. S.O Pillai, "Solid State physics" Anna University Madras. Ch-5, pp.186-189
2. Charles Kittel, "Introduction to Solid State Physics" John Wiley & Sons, Singapore, New York, seventh edition, Ch.13, PP.379-414(2007).
3. O.Garcia-Zaldivar et.al. Relaxor Behaviour in Ferroelectric Ceramics. <http://dx.doi.org/10.5772/52149>
4. Kwan Chi Kao, "Dielectric Phenomena in Solids. Elsevier Academic Press.
5. "Ferroelectric ceramics: Processing, properties & applications" Ahmed Safari, Rajesh K. Panda and Victor F. Janas, Department of Ceramic science and Engineering, Rutgers University, Piscataway NJ 08855, USA
6. Xu Y. Ferroelectric Materials and Their Applications. Netherland: Elsevier Science Publishers ;(1991).
7. Mailadil T. Sebastian Dielectric Materials for Wireless Communication.Ch-6(ABO_3 type perovskite), Elsevier Academic Press
8. Zukifli Ahmad. Polymer Dielectric Materials. Ch.1,DOI: 10.5772/50638
9. Robert Shaw. Dissemination of IT for the Promotion of Material Science(DoITPoMS)
10. Pawan Kumara, Seema Sharma, O.P. Thakurb, Chandra Prakashb, T.C. Goela. Dielectric, piezoelectric and pyroelectric properties of PMN-PT (68:32) system. *Ceramics International* 30 (2004) 585–589
11. A. Fundora, A. V.azquez, J. Portelles, F. Calderon, J.M. Siqueiros. Diffuse phase transitions in ferroelectric ceramics. *Journal of Non-Crystalline Solids* 235±237 (1998) 567±569
12. Wei J, Hawley M, Assmussen J. Microwave power absorption model for composite processing in a tunable resonant cavity. *Journal of Microwave Power and Electromagnetic Energy* 1993;28(4):234–242.
13. Thostenson ET, Chou TW. Microwave processing of thick-section polymer composites. *Proceedings of the 12th Annual Technical Conference of the American Society for Composites, Dearborn, Michigan.* pp. 931–940.
14. Halil Guler, Figen Kurtulus. A microwave assisted route for the solid state synthesis of lead pyrophosphate. *Journal of Materials Science.* 40(2005) 6565-6569
15. M. Hinterstein, S.-T. Zhang et.al. Determination of the superstructure of lead free piezoelectric ceramics (BNT-BT-KNN), Materials Science Darmstadt University of Technology, Petersenstr. 23, 64287 Darmstadt, Germany
16. S.-T. Zhang, A. B. Kounga, E. Aulbach, H. Ehrenberg, J. Rödel, *Appl. Phys. Lett.* 91 112906 (2007)
17. Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takator, T. Homma, T. Nagaya, M. Nakamura, *Nature (London)* 432, 84 (2004)
18. Shan-Tao Zhang, Feng Yan et.al. Phase diagram and electrostrictive properties of $Bi_0.5Na_0.5TiO_3$ – $BaTiO_3$ – $K_0.5Na_0.5NbO_3$ ceramics, *Applied Physics Letters* 97, 122901 (2010)