Studies of Structural, Microstructural and Electrical properties of Barium Titanate Modified Lead Iron Niobate

Thesis submitted in partial fulfilment
of the requirements for the degree of

Master of Science (M. Sc.) in Physics

Under the academic Autonomy
National Institute of Technology, Rourkela

By

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Roll No: 411PH2106

Under the guidance of

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Certificate

This is to certify that the work in the thesis entitled "***Studies of structural, microstructural and electrical properties of Barium Titanate modified Lead Iron Niobate***." submitted by **Ms. Sritama Pal** is a record of an original research work carried out by her under my supervision and guidance in partial fulfilment of the requirements for the award of the degree of Master of Science in Physics. This thesis has not been submitted for any degree or academic award elsewhere.

Dr. Dillip K Pradhan

Asst. Professor

Department of Physics,

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DECLARATION

I hereby declare that the work carried out in this thesis is entirely original. It was carried out by me at Department of Physics, National Institute of Technology, Rourkela. I further declare that it has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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Acknowledgment

Firstly I would like to express my sincere gratitude to my project supervisor Dr. Dillip K Pradhan. I am thankful to him for his kindness, motivation and valuable suggestions throughout my project.

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Abstract

One series of Barium Titanate ($BaTiO_3$) modified Lead Iron Niobate ($Pb(Fe_{0.5}Nb_{0.5})O_3$) ceramic oxides having chemical formula $(1-x)\ Pb(Fe_{0.5}Nb_{0.5})O_3 - x\ BaTiO_3$ ($x = 0.00, 0.025, 0.05, 0.075, 0.1$) were prepared by solid state reaction route. The formations of the compounds were confirmed by X-ray diffraction analysis. Rietveld refinement result of X-ray diffraction spectra confirm that all the compositions crystallize in monoclinic crystal structure with *Cm* space group. FESEM micrographs show a decrease in average grain size on increasing composition. Dielectric properties of the materials were studied in a wide frequency range at different temperatures. The temperature dependent dielectric study showed the ferroelectric to paraelectric phase transition around 110 °C for $Pb(Fe_{0.5}Nb_{0.5})O_3$ and decreases on increasing composition.

Contents

1. Introduction:

Multiferroic materials have become an important field of research to be studied extensively due to its interesting physical properties and varied multifunctional device applications such as multiple state memory, sensors, multilayer capacitors, actuator, electro-optic and acoustic-optic devices [1]. Crystals are said to be multiferroic when two or more primary ferroic order parameters are found in the same phase [2]. The primary ferroic order parameters are ferroelectric, ferromagnetism and ferroelastic ordering. Multiferroic materials have also ability to couple electric and magnetic order parameters, thus provides a new dimension in designing devices. The diagram given below showing the existence of different ferroic order parameters and their relation in multiferroics.

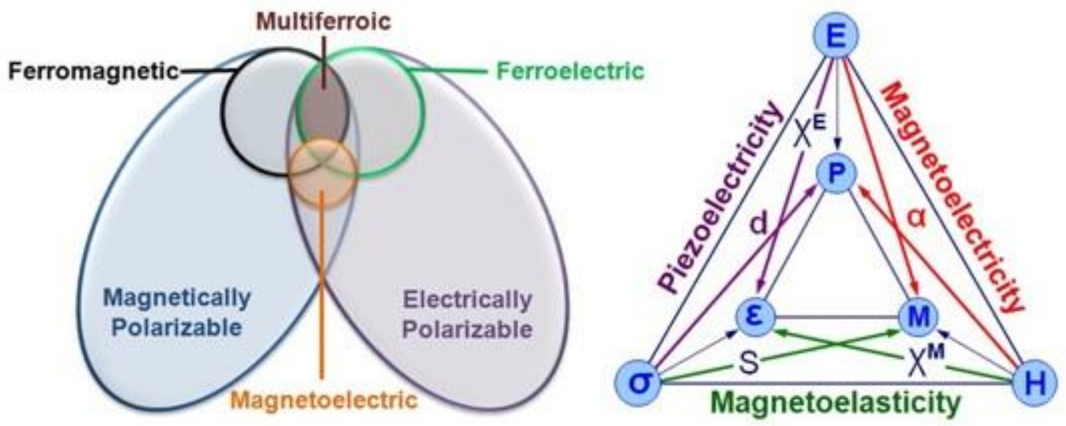


Fig 1: Multiferroics: existence of different primary ferroic parameters and inter relationship [2].

1.1 Ferroelectricity

We can define a set of materials as ferroelectric materials if they possess spontaneous polarisation (i.e. they have a net electric dipole moment without application of external electric field) below certain temperature. The corresponding temperature is called ferroelectric transition temperature or Curie temperature (T_C). Above the transition temperature, the material loses spontaneous polarisation, thus also losing ferroelectric property. This high temperature phase is called paraelectric state. In the ferroelectric samples, the centre of positive charges do not coincides with that of negative charges thus giving rise to a net dipole moment and spontaneous polarization. Hysteresis loop (i.e., plot of polarisation vs electric field) is the characteristics properties of ferroelectric material as shown in Fig. 2(a), where P_s = saturation polarisation, P_r = remenent polarisation and E_c = coercive field.

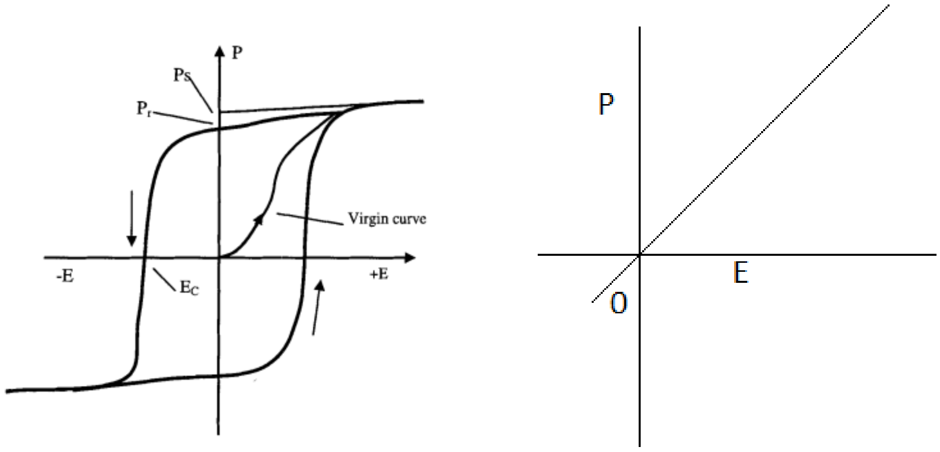


Fig.2 (a): ferroelectric material (b): paraelectric material

The shape and size of the hysteresis loop for a particular sample is a function of temperature. With increase in temperature, the width and the height of the hysteresis loop decreases i.e, the remnant polarisation and coercive field decreases, or the ferroelectric properties of a sample decreases. At the transition temperature, it merges to a straight line which shows the absence of ferroelectric property as shown in Fig. 2 (b). At this temperature the specimen becomes paraelectric.

Depending upon the type of phase transitions, ferroelectric materials are broadly classified into the following two groups: (i) order – disorder 2) displacive phase transitions [3]. In the first type, the transition is associated with the ordering of the ions. It includes the crystals having hydrogen bonds in which ferroelectric property is related to motion of protons. Above the Curie temperature, the proton distribution along the hydrogen bond is elongated symmetrically, thus resulting absence of ferroelectric behaviour. But below the Curie temperature, the distribution is asymmetric, rather concentrated with respect to neighbouring ions. Thus one end of the bond is preferred by the protons than the other. This gives rise to a dipole moment. In the second type, that is displacive ferroelectric materials, the transition is associated with the ordering of the whole sub lattice of ions of one type relative to another sub lattice of ions of the other type, thus separation in centre of charges occurs giving rise to a net dipole moment [3].

1.2. Ferromagnetism

The characteristic feature of ferromagnetism and ferromagnetic order is spontaneous magnetisation M_s, which is indicated by a magnetic moment even in zero applied magnetic fields. This is caused due to spontaneous alignment of atomic magnetic moments. This disappears on heating above a critical temperature known as the Curie temperature T_C [9, 3].

1.3. Ferroelasticity

Ferroelasticity can be understood as the mechanical equivalent of ferroelectricity and ferromagnetism. Ferroelasticity is a phenomenon in which a material may exhibit a spontaneous strain. Above a certain temperature T_c, it undergoes phase transition and the deformation due stress applied is completely recovered [2]

1.4. Types of multiferroics:

There are two groups of multiferroics:

(a) Type-I multiferroics: This class of multiferroic materials possess ferroelectric and anti/ferromagnetic ordering in a single phase but both the ordering are independent of each other. In these cases, although the sources of ferroelectricity and ferromagnetic ordering are different, but there is some coupling between these two phenomena exist. Ferroelectric phase transition temperature is observed at relatively higher temperature than magnetic ordering transition temperature.

(b) Type –II multiferroics: In this class of materials ferrroelectricity causes ferromagnetic ordering and vice-versa. Thus there exists a strong coupling between the two phenomena.

There are very less number of multiferroic materials existed in nature due to chemical incompatibility and mutual exclusiveness of ferroelectric and ferromagnetic ordering. The details are explained below:

i. **d^0 vs d^n :** The partially filled d and f shells of the transition metals or rare earth metals causes the microscopic origin of magnetic ordering, whereas, the origin of ferroelectric ordering is due to the metal ions having empty d orbital. So both the phenomena are contradicting each other indicating the difficulty to be existed in a single phase. One way to overcome this problem is to make “mixed” perovskites with d^0 and d^n ions at the B-site of perovskite [2].

ii. **Symmetry consideration:** A basic requirement for the existence of ferroelectricity is non-centrosymmetric phase (i.e., the presence of non-coincident of centre of positive and negative charges creates net dipole moment), and thus allows a permanent electric polarization. Out of 32 point groups, 21 classes are non centrosymmetric, out of which 20 are piezoelectric. Only 10 out of these permits existence of pyroelectricity. Ferroelectrics may be considered as subgroup of pyroelectricity. Whereas only few (11) point groups exhibits ferromagnetic ordering [11].

iii. **Electric properties:** The ferroelectric samples are usually electrically insulators. Otherwise, if we apply an electric field, the sample will conduct and an electric current will flow through it rather than inducing polarisation. Ferromagnetic samples though do not require having specific electrical properties, are often metals. For example, the elemental ferromagnets Fe, Co, and Ni and their alloys are metallic. Therefore, as occurrence of insulating character and metallicity in the same sample is impossible, thus simultaneous coexistence of ferroelectric and ferromagnetic oredering in the same phase is difficult.

So, multiferroics are rare in nature.

Although multiferroics are rare in nature but there are few multiferroics exists such as $Pb(Fe_{0.5}Nb_{0.5})O_3$, $Pb(Fe_{0.5}Ta_{0.5})O_3$, $BiFeO_3$, $BiMnO_3$, $BaMnO_3$ etc[2]. Although multiferroic oxides belong to different structure, perovskite structured compounds are more widely studied. The above mentioned multiferroics are belongs to perovskite structure.

1.5. Perovskite structure

Perovskite structure generally represented by the chemical formulae ABO_3, where A and B are cations and O is the anions. The ionic radii of B cation are smaller in size than A. It is an FCC derivative structure in which A (at the corner of the cube) and O (at the face of the cube) together forms FCC lattice, while B cation occupies the centre of the cube in the FCC array. A cation possesses 12-fold coordination number, whereas B cation has 6-fold coordination number surrounded by the octahedron of oxygen anion.

The stability and nature of a perovskite crystal is determined by the value of Goldschmid tolerance factor (t), which is given by the relation:

$$\boxed{t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)}}$$

Where, R_A = radius of the cation A, R_B = radius of the cation B, R_O = radius of oxygen anion.

There are three possible values of ‘t’: (1) $t \geq 1$: In this case, there will be displacive distortion within the BO_6 octahedral giving rise to a dipole moment .Thus the perovskite will show ferroelectricity. (2) $t < 1$: This refers to a tilting or rotation of the BO_6 octahedron resulting to an antiferroelectric perovskite. (3) $t = 1$: This is for an ideal perovskite.

Barium titanate ($BaTiO_3$) is one of the well-known perovskite structures. In this case barium (Ba) ions occupy the corners of a cube as being larger in size, the centres of the cube faces are occupied by oxygen (O) ions. The octahedron formed by the oxygen ions contains titanium (Ti) ion at its centre. The structure is stable cubic structure above 120^{o}C. In this stage, the centre of the negative charge and positive charge coincide, so that there exists no spontaneous dipole moment. But if it is cooled to a temperature below 120^{o}C, then the highly charged titanium ion shifts to one side of the body centre, and the crystal transforms to tetragonal crystal structure. The titanium ion contributes to high polarizibility due to the following reasons: (i) It has positive charge which ionises as $Ti^{+4.}$ (ii) As it is very smaller in size, it gets more space inside the oxygen octahedron to be displaced over relatively a large distance. (iii) All the ferroelectric samples having perovskite structure contain at least one transition metal ion having empty d shell. Ferroelectric phenomenon in such systems is caused by the off-center shifts of the transition metal ion. These transition metal ions form strong covalent bonds with the oxygens of the BO_6 octahedral, which resulted in shifting of the transition metal ion from its centre. This forms a partial charge separation thus giving a net dipole moment and spontaneous polarization.

During last few years, it is noticed that PFN has been studied to find its suitability to be used in various electronic devices due to its high dielectric constant (>10000), diffuse phase transition behaviour, low sintering temperature for synthesis and multiferroics properties. PFN is a multiferroics belong to perovskite structure (Fig. 3), having ferroelectric and antiferromagnetic orderings.

Lead iron niobate $[Pb(Fe_{0.5}Nb_{0.5})O_3]$ belongs to lead based perovskite structure having lead ions at the corners of the cube, the centres of the faces of the cube are occupied by oxygen ions. The centre of the oxygen octahedron is occupied and shared by both ferrite ion and niobate ion as shown in Fig. 3.

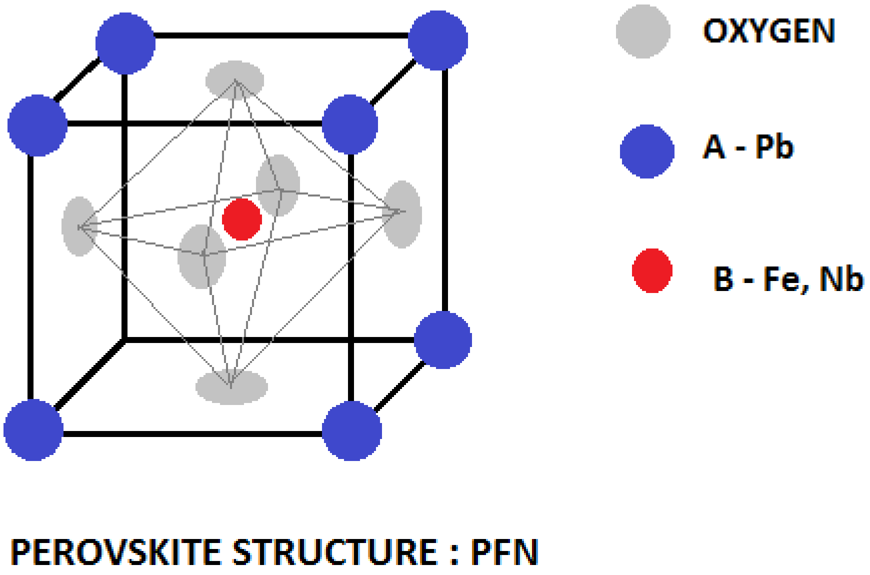


Fig 3: Arrangement of ions in PFN perovskite structure.

1.6. Literature survey of some PFN based materials.

Recent years have witnessed enormous interest in multiferroic materials due to their potential applications in memory, sensor, and actuator devices. [4]

It is reported by different research group that PFN crystallize to monoclinic (!)/Rhombohedral (!) crystal structure. Its curie temperature is 373 K and Neel temperature at 143 K [7]. The observed value of spontaneous polarisation is relatively large as compared to other multiferroics.

It has been reported that the ferroelectric to paraelectric phase transition temperature of PFN decreased on increasing Barium concentration in the sample. The magnetic measurements suggested that PFN and barium doped PFN are paramagnetic at room temperature, having weak magnetisation at low temperature (i.e., ≤ 15 K). [10]

Majumdar *et al.* [12] reported the ferroelectric transition temperature of PFN to be around 370K from temperature dependant loss tangent and capacitance at different frequencies.

Jie Wang *et al.*[13] studied single crystal 0.94($PbFe_{1/2}Nb_{1/2}O_3$)–0.06($PbTiO_3$), grown by the Bridgman method and reported that no sign of the presence of Curie temperature between room temperature and 300 °C was noticed. They exhibited very high dielectric constant of the order of 10^5 at frequency lower than 100 kHz.

O. Raymond *et al.* [14] fabricated PFN starting from oxide reagents and different kinds of $FeNbO_4$ precursors with either monoclinic or orthorhombic structures. Deviations in the degree of diffuseness, densities and grain size were observed depending on the kind of precursor.

Sahoo *et al.* reported that when Yttrium is substituted in PFN, it resulted in notable enlargement of room temperature remnant polarization [5]. Moreover, the compounds showed a negative temperature coefficient of resistivity type behaviour as that of a semiconductor.

There are some inherent problems usually encountered with PFN:

1) It is difficult to synthesize single phase of PFN. While synthesizing PFN by solid state reaction route, pyrochlore phases ($Pb_3Nb_4O_{13}$ or $Pb_2Nb_2O_7$) with lower dielectric constant always coexists with the desired phase. Thus it may lower the net dielectric constant of the resulting sample.[1]
2) In PFN, iron exists in both +3 and +2 oxidation state, which gives rise to increase in conductivity. The occurrence of oxygen ion vacancies during sintering causes increase in conductivity, dielectric loss and space charge accumulation at the interfaces. All these contributions result in lower resistivity and makes it very difficult to pole and measure polarisation hysteresis characteristics.
3) Till now there are controversial reports on the crystal structure of PFN. Both rhombohedral (R3m) and monoclinic (Cm) structures are being reported by different researcher [12]. Rhombohedral structure with space group R3m has been reported by Yang.*et.al* [8]. Singh.*et.al* reported evidences of monoclinic structure with Cm space group [1]. Rhombohedral R3m space group has been reported by R.K.Mishra.*et.al* [15].

In order to overcome the above mentioned problems; various methodologies such as (i) substitution at A and/or B sites, (i) fabrication of solid solution with different perovskites

(iii) preparation of nano sized single phase materials using different synthesis route have been adopted around the globe. In the present study, we have planned to fabricate the solid solution of PFN with $BaTiO_3$.

2. Material to be investigated:

$(1-x)$ $[Pb(Fe_{0.5}Nb_{0.5})O_3]$ + x $(BaTiO_3)$ with $x = 0.0, 0.025, 0.05, 0.075, 0.1$

3. Objectives of the project:

1) The aim of this project is to synthesize new complex multiferroic samples i.e., $(1-x)$ $[Pb(Fe_{0.5}Nb_{0.5})O_3]$ + x $(BaTiO_3)$ by solid state reaction route.

2) To study the structural, microsrtuctural and electrical properties of the samples using XRD, FESEM and Dielectric characterisation techniques.

3) Attempt will be made to find out the exact crystal structure of pure PFN using Rietveld refinement.

4. Synthesis of the samples:

Ceramics are very important materials because of their varied direct and indirect uses in various fields of science and engineering along with in daily life. These are inorganic and non-metallic materials formed by the action of heat and subsequent cooling or sometimes by the action of simultaneous heat and pressure. Generally, these materials comprise of at least two elements out of which, one is a non metal. These may be crystalline or partly crystalline. Their efficient synthesis of ceramic materials is of great importance. In the present study, we are dealing with electro-ceramics. There are some techniques for the synthesis of electroceramics such as solid state reaction route, high energy ball milling, soft chemical route, hydrothermal crystallisation etc. Each method is having some advantages and disadvantages in respect of the quality of the sample produced, time duration, economy etc. In view of this, solid state reaction route is found to be much simpler and cost effective, also suitable for this case.

4.1 Solid state reaction route:

This method is widely used for synthesis of polycrystalline solid sample from solid starting materials.

Solid starting materials do not react at room temperature to form the desired compound. Therefore they are heated at very high temperature and this high temperature enables the flow of atoms trough the solids at a sufficient rate, thus the desired compound is obtained. A number of procedures are followed before heating to reduce the time needed for synthesis. The starting materials are grounded together to ensure good mixing and increasing contact between the grains which will react. They are also grounded together in liquid medium (acetone) to enable a more homogenous and uniform mixing.

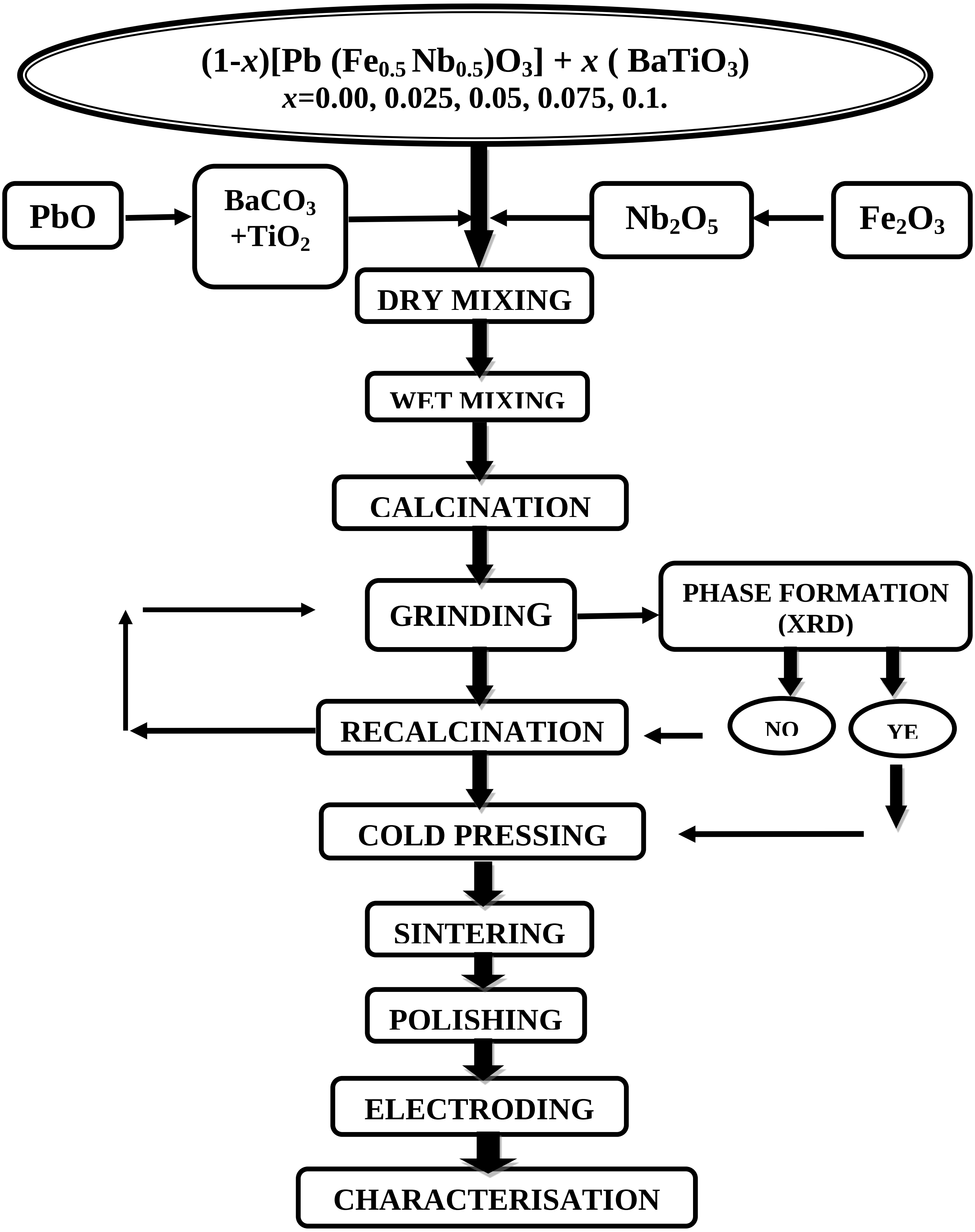
4.2 Experimental steps:

1) For preparation of PFN, high purity oxides (PbO, Nb_2O_5, Fe_2O_3) were weighed as per the calculated stoichiometric ratio and grounded together in agate mortar and pestle (previously cleaned by acetone) for one hour. Then acetone was added to the mixture and again grounded for two hours till the mixture dries up completely. Extra 3% of the lead oxide was added to compensate the loss during calcination.

2) For the preparation of solid solutions, the calculated amount of pure $BaCO_3$ and TiO_2 were added along with the calculated quantities of PbO, Nb_2O_5, Fe_2O_3. Extra 3% of PbO was also added. This mixture was again grounded by maintaining the same above procedure.
3) All the samples including pure PFN (x=0.00, 0.025, 0.05, 0.075, 0.1) were calcined at 1000^0C and air atmosphere for six hours in separate crucibles covered by lids. After calcination, lumps were formed and subsequently it was grounded to make powder to confirm the phase formation. The lumps were brittle and the property was noticed to be increasing with increase in the compositional value of *x*. The calcined powders were found to be little brownish as compared to brick red (before calcination).
4) Phase formation of each samples were checked by XRD at room temperature.
5) Then, the calcined powders of each compound were mixed properly with polyvinyl alcohol, which acts as a binder. It gives some mechanical strength to the pellets formed out of it. It also reduces the brittle nature of the pellets. About 1-2 mm thick cylindrical pellets were prepared from the above powders by uniaxial pressing using a hydraulic press at 6×10^7 kg/m^2 pressure.
6) Sintering of the pellets of each samples were carried out at atmospheric pressure and temperature of 1050^0C for six hours, in air atmosphere. This leads to better compaction and pore elimination of the samples. The binder is burnt out during high temperature sintering.

The sintered pellets were polished by emery paper and painted with silver paste which acts as electrode for electrical measurements.

The flowchart for the steps of preparation of the samples:



5. Characterisation:

After preparation of the synthesis of materials, different experimental techniques with wide experimental conditions were adopted to characterize the materials. The principles of the experimental techniques are given below:

5.1. X-ray diffraction (XRD)

XRD technique is very important, reliable and non destructive method to characterize, and analyze the crystalline structure of the sample. This method is based on the principle of diffraction phenomena. In this experiment, x-rays are used as probe, since it’s wavelength compared to the spacing between the lattice planes which is an important condition for diffraction.

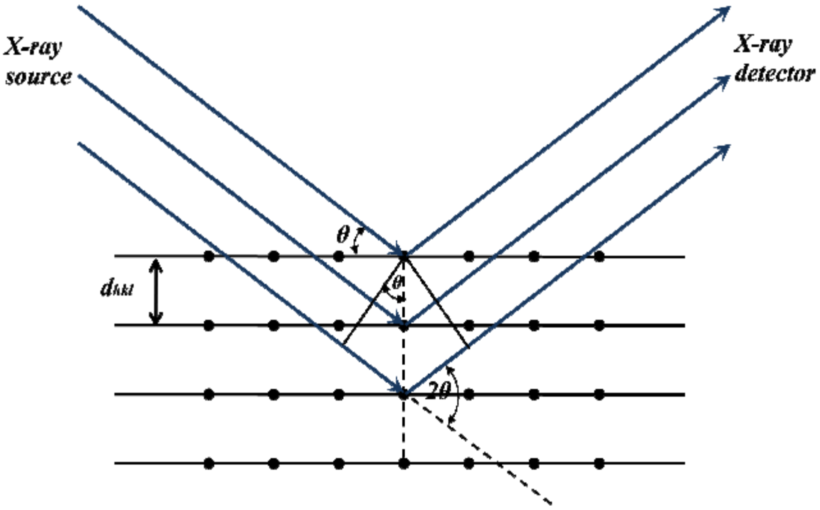


Fig 4:X-ray diffraction by crystallographic planes.

The diffraction condition satisfies Bragg equation given by equation:

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

Where, d = spacing between two consecutive lattice planes, θ = incident angle of the X rays, λ = wavelength of X ray

The qualitative and quantitative information about the phase formation and structure of the material obtained from an XRD pattern is a direct result of the following things:

(1) The positions of the diffraction peaks are the result of the shape and size of the unit cells in the crystal.

(2) Lattice constants can be determined from the positions or d spacing and can be represented by a general formula

$$\mathbf{1/d^2_{hkl} = V^2\,[\,h^2b^2c^2\sin^2\alpha\ + k^2c^2a^2\sin^2\beta\ + l^2a^2b^2\sin^2\gamma\,]}$$

Where; V = volume of the unit cell, $\mathbf{V = abc\,(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + \cos\alpha\cos\beta\cos\gamma)\ ½}$

Here **a, b, c, α, β** and **γ** are lattice parameters and angles and **h, k, l** denotes the miller indices of the crystallographic planes. The formula given above is generally used to calculate lattice parameters.

5.2. Field emission scanning electron microscopy (FESEM):

It is a powerful technique to study the topography, morphology and composition of the materials with much higher resolution. This is a microscope using electron beam as the probe. Its principle of operation can be understood as a modified version of scanning electron microscope, in which a field-emission cathode in the electron gun is introduced. This provides a narrower probing beam at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. When a beam of highly energetic electrons strikes the sample, the secondary electrons, x-rays and back-scattered electrons are ejected from the sample. These electrons are then collected by the detector and convert into signal that displays on a screen.

It has many advantages like it produces clearer, less electrostatically distorted images with spatial resolution 3 to 6 times better (1.5 nm) than conventional SEM. In the present study, the FESEM micrograph was taken using NOVA- NANO SEM 450, with different magnifications. As the samples are non-conducting, a thin layer of gold is coated.

5.3. Dielectric property Measurements:

A good dielectric is, of course, necessarily a good insulator but the converse is not possible. Studies of dielectric properties of a materials helps to understand about the behaviour of localized electric charge carriers and the mechanism of different electrical polarization phenomena in the material. When a dielectric material is subjected to an external electric field, electric dipoles are induced in the material and thus it becomes polarized. The polarization can be defined as dipole moment per unit volume. The polarization is directly proportional to the macroscopic electric field i.e.

$$\mathbf{P} = \alpha \mathbf{E}$$

Here, α: the polarizabilty of atoms and molecules, P: polarization, E: electric field

There are different types of polarization existed in dielectric materials such as (i) Space charge polarization, (ii) Dipolar polarization, (iii) Ionic polarization and (iv) Electronic polarization

The frequency dependence of polarization can be understood from the following figure:

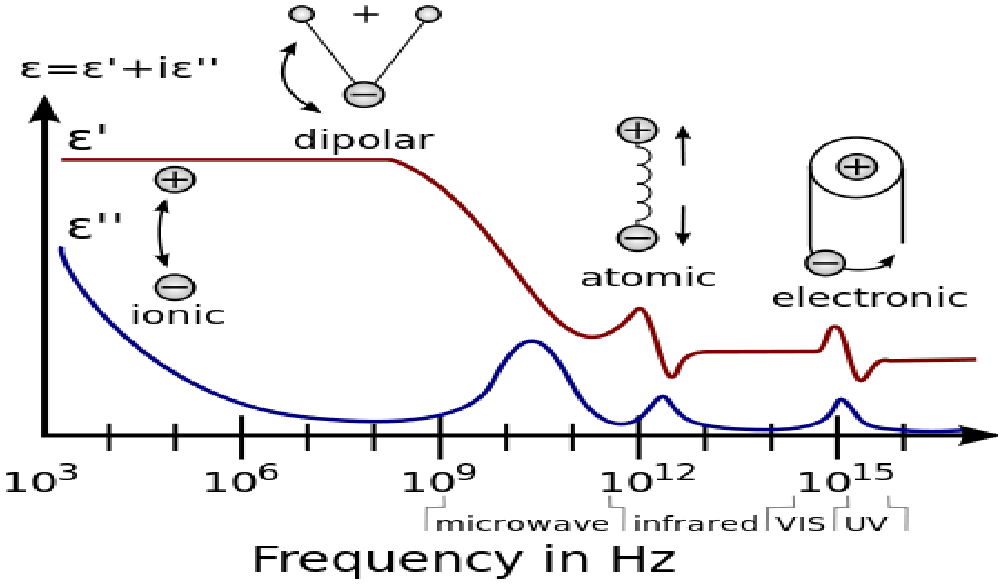


Fig 5: frequency dependence of dielectric constant.

When a dielectric is subjected to the ac voltage, due to frequent change of frequency, some electrical energy is absorbed by the material and is dissipated in the form of heat. The dissipation is called dielectric loss (tanδ).

6. Results and discussions:

6.1. XRD analysis

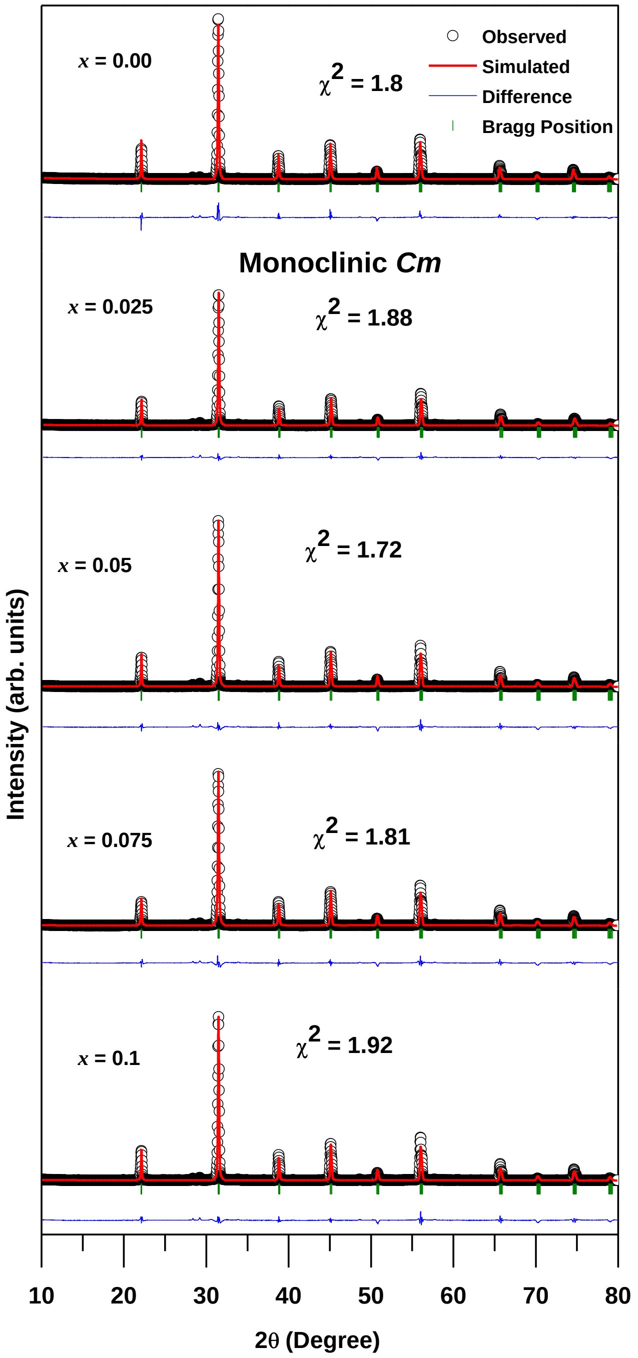


Fig. 6 Rietveld refined X-ray diffraction patterns of (1-x) $Pb(Fe_{0.5}Nb_{0.5})O_3$ -x $BaTiO_3$ with different values of *x* = 0.00, 0.025, 0.05, 0.075, 0.1 at room temperature.

Fig. 6 compares the room temperature XRD patterns of calcined powder of (1-x) $Pb(Fe_{0.5}Nb_{0.5})O_3$ -x $BaTiO_3$) for (x= 0.00, 0.02, 0.04, 0.06, 0.08). The structural analysis was carried out by Rietveld refinement using FULLPROF package. The shapes of peaks were modelled using pseudovoigt function and background was modelled using six coefficient polynomial function. During refinement process, global parameters such as zero factor, scale factor, profile shape parameter, (U V W), asymmetric parameters, lattice parameter and atomic position were varied. The occupancy of all the atoms was kept fixed during refinement process. For pure PFN i.e. x = 0.00, a good match is observed between the experimental data (symbol) and theoretical (line) as shown in Fig.6, suggesting the correctness of choosing the monoclinic structure with space group Cm. The XRD patterns of all the $BaTiO_3$ modified samples are similar to PFN. Therefore all the compositions have been refined with the same space group Cm and good match is observed. Moreover, the peak observed around $2\theta = 27^0$ for pure PFN indicating the presence of secondary phase and it decreases with increase in composition. Calculated values of the lattice parameters a, b, c and β are tabulated in Table: 1. The variation of unit cell parameters as function of composition has been displayed in Fig.7 and 8.

Table: 1

composition (x)	a (Angstrom)		b (Angstrom)		c (Angstrom)		β (degree)	
	obs.value	error(±)	obs.value	error(±)	obs.value	error(±)	obs.value	error(±)
0.00	5.6744	0.00152	5.6708	0.00149	4.0165	0.00105	89.897	0.00488
0.025	5.67159	0.00114	5.67875	0.00112	4.02093	0.00083	89.88857	0.00294
0.05	5.67563	0.00127	5.68291	0.00125	4.02366	0.00093	89.88357	0.00297
0.075	5.67592	0.00139	5.68459	0.00138	4.02548	0.00098	89.86266	0.00301
0.1	5.67585	0.0015	5.68253	0.00155	4.02195	0.0011	89.88628	0.00292

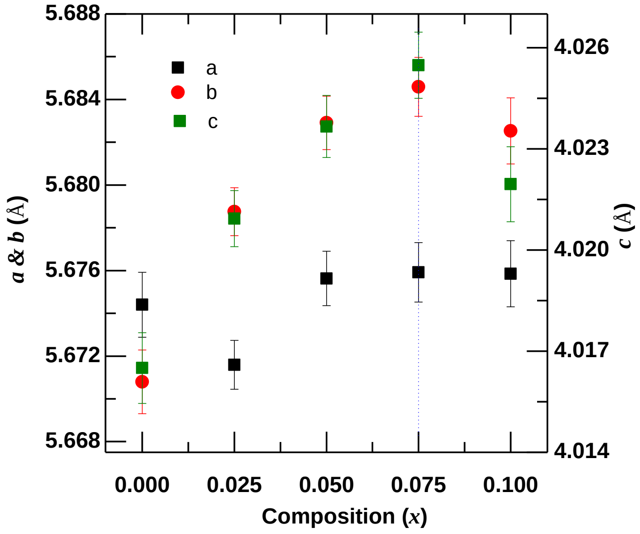


Fig: 7-variation of lattice parameter (a, b, c) with increasing composition *x* .

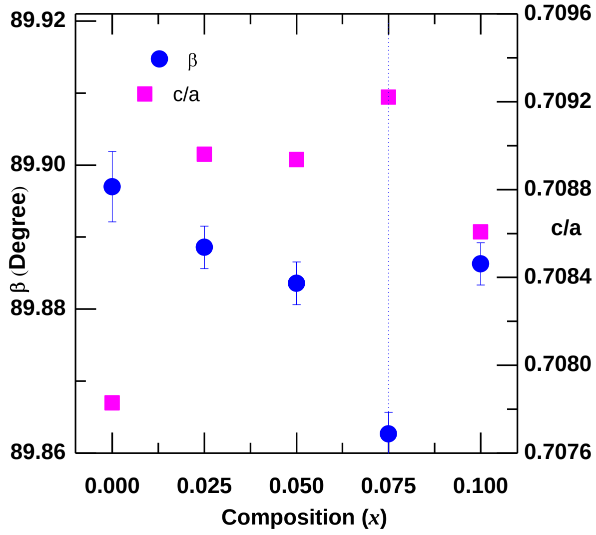


Fig: 8-variation of β and c/a with increasing composition *x*.

6.2. FESEM:

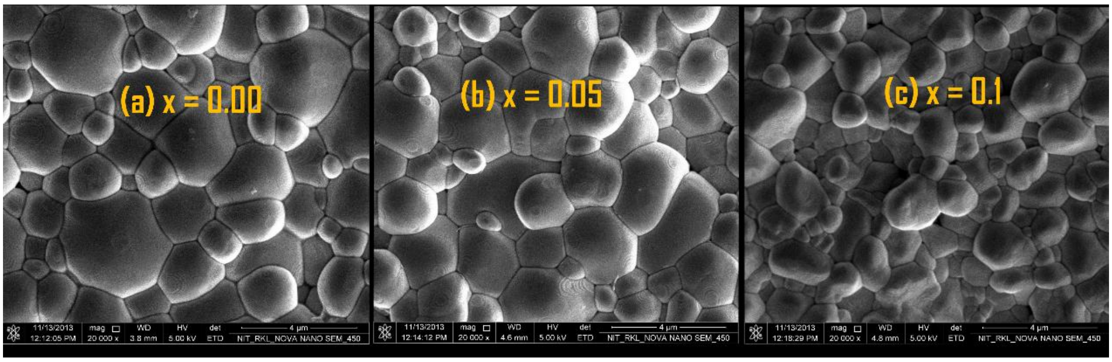


Fig: 9- FESEM micrographs of (1-x) $Pb(Fe_{0.5}Nb_{0.5})O_3$ -x $BaTiO_3$ with (a) x=0.00, (b) x=0.05, (c) x=0.1

Fig.9 shows the FESEM micrographs of (a) x=0.00, (b) x=0.05, (c) x=0.1. It is observed that the grains of different sizes varying from 1-2 μm are inhomogeneously distributed throughout the sample. The grain and grain boundary are well distinct and clearly visible. There are minimum no. of pores between the grains are observed thus, the synthesized sample is high degree of density. The average grain size decreases with increase in composition *x*.

6.3. Dielectric study:

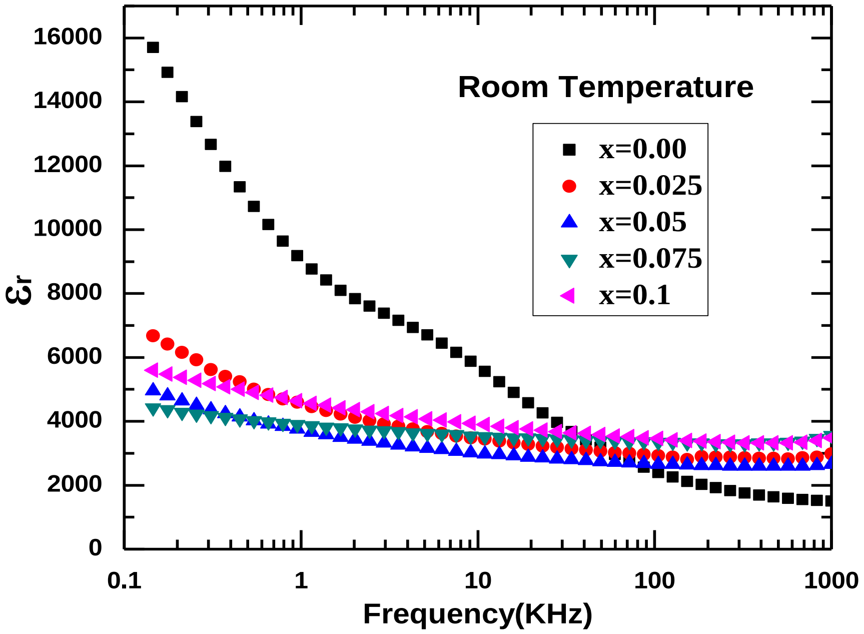


Fig 10: Frequency dependent dielectric permittivity for different compositions (x=0.00, 0.025, 0.05, 0.075, 0.1) at room temperature.

Fig. 10 shows the variation of dielectric permittivity with frequency for different value of *x* =0.00, 0.025, 0.05, 0.075, 0.1 at room temperature. From the above figure, it can be observed that the dielectric permittivity decreases with increasing frequency for each of the samples along with pure PFN. This characteristic is the signature of polar dielectric materials.

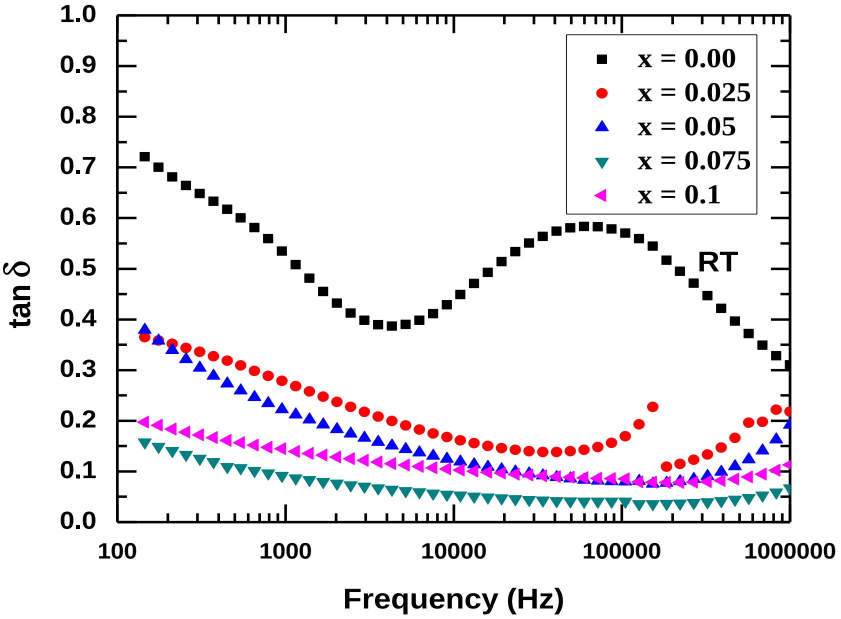


Fig 11: Frequency dependant dielectric loss for all the compositions (x=0.00, 0.025, 0.05, 0.075, 0.1) at room temperature.

Fig. 11 shows the variation of dielectric loss with frequency for different value of *x* at room temperature. The dielectric loss decreases with increase in frequency except pure PFN. In pure PFN the dielectric loss decreases first then there is appearance of peak at higher frequency side. The dielectric loss of $BaTiO_3$ modified PFN is less as compared to pure PFN.

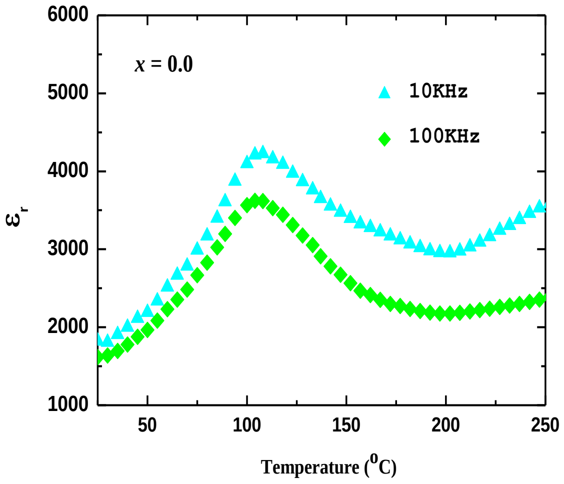


Fig: 12 (a)

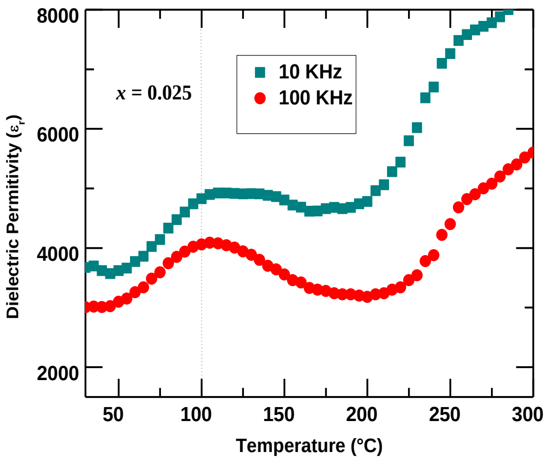


Fig: 12 (b)

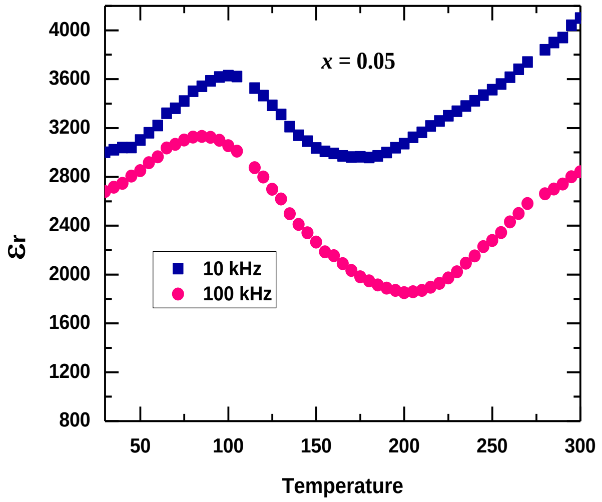


Fig: 12 (c)

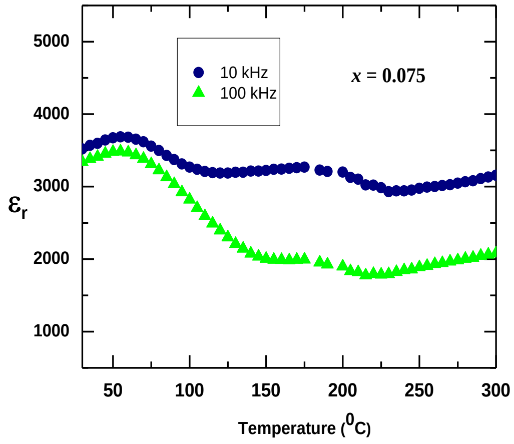


Fig: 12(d)

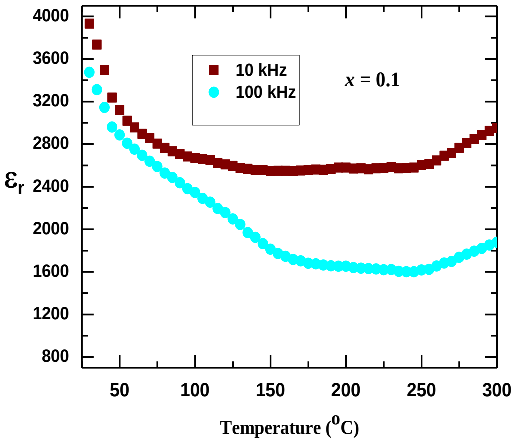
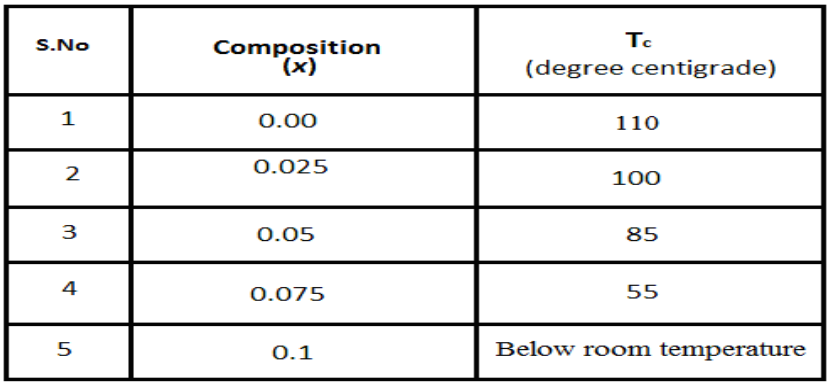


fig: 12(e)

Fig12 (a, b, c, d, e): variation of dielectric permittivity with temperature at different frequencies for all the compositions (x=0.00, 0.025, 0.05, 0.075, 0.1)

Figure 12 shows the variation of dielectric permittivity with temperature at different frequencies for all values of x. The dielectric permittivity is found to be increasing with temperature, attains a maximum value, and then decreases with further increase in temperature. The temperature corresponding to maximum value of ε_r is called ferroelectric transition temperature. The temperature above the transition temperature the sample becomes paraelectric, and below transition temperature it happens to be ferroelectric. The transition temperature of pure PFN has been found to be around 110^0C and it is decreasing with increasing value of *x*. This can be explained as the suppression of ferroelectric behaviour caused by substitution of Pb^{2+} in PFN by Ba^{2+} ion. It is also noticeable that at composition of 10% the transition temperature drops to below room temperature ($<30^0$C). The variation of transition temperature with composition is fiven in Table 2

Table 2: comparison of ferroelectric transition temperature (T_c) of various compositions (x=0.00, 0.025, 0.05, 0.075, 0.1)



S.No	Composition (*x*)	T_c (degree centigrade)
1	0.00	110
2	0.025	100
3	0.05	85
4	0.075	55
5	0.1	Below room temperature

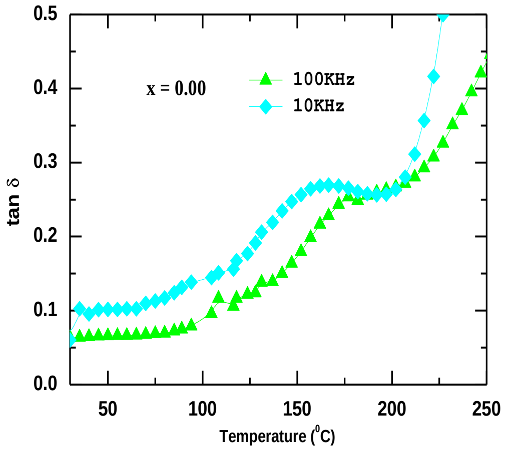


Fig: 13(a)

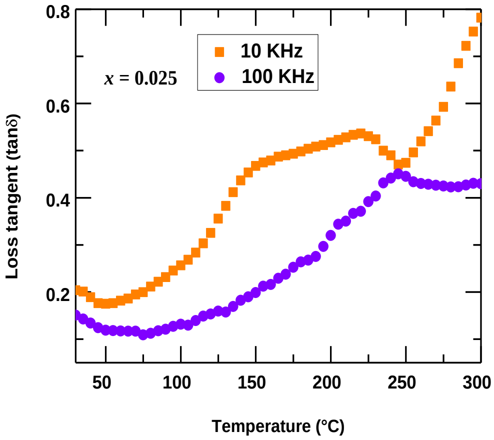


fig: 13(b)

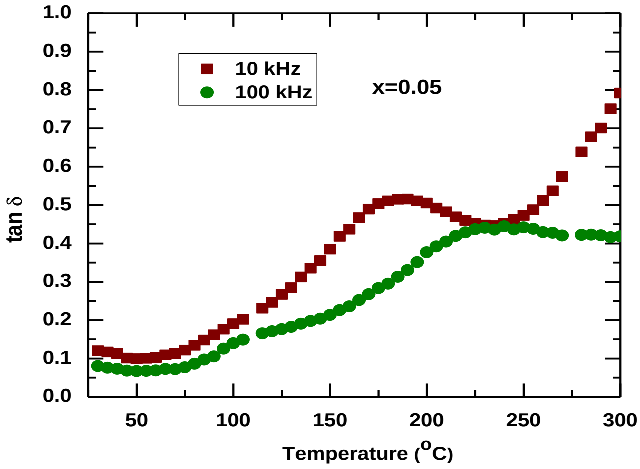


Fig: 13(c)

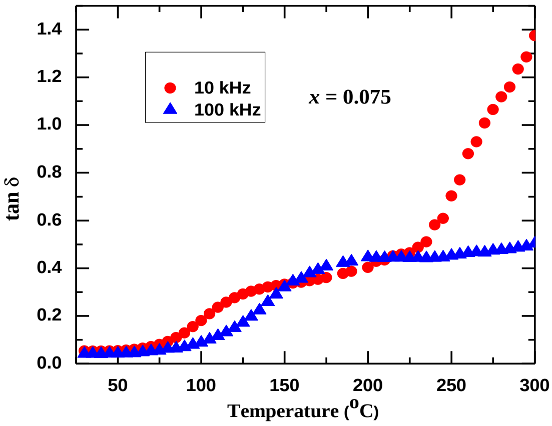


Fig: 13 (d)

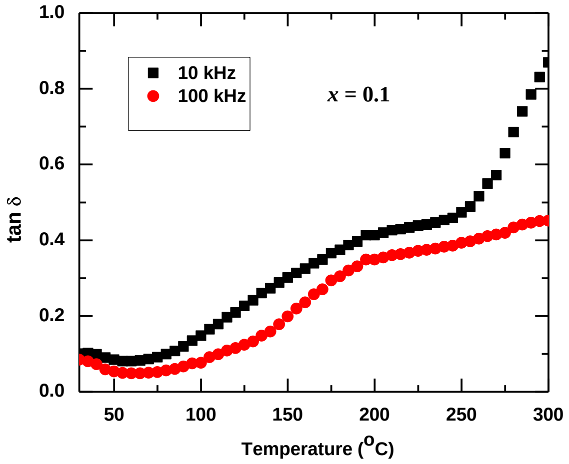


fig: 13(e)

Fig13 (a, b, c, d) shows the temperature dependent of dielectric loss at frequencies10 KHz and 100 KHz for all the compositions (x=0.00, 0.025, 0.05, 0.075, 0.1).

Figure 12 shows the variation of variation of dielectric loss with temperature at different value of x. It is observed that dielectric loss increases with increase of temperature. Moreover, it decreases with increase in concentration up to x=0.075, and then increases with further increase of composition. Above temperature around 250^0C, tan δ increases sharply which can be attributed to increase in conductivity at high temperature.

7. Conclusions:

In the present investigation, Barium Titanate modified Lead iron niobate perovskite ceramics have been prepared using high temperature solid state reaction route. The structural (XRD), microstructural (FESEM) and dielectric properties of the proposed compounds have been studied extensively.

Based on the results obtained, following conclusions have been made:

1. X-ray diffraction (XRD) studies confirmed the formation of the compounds with monoclinic crystal system having Cm space group. The lattice parameters (a, b, c) are found to be increasing with increase of composition up to x=0.075, and then decreases with further increase in composition. However, the lattice parameter β is observed to be decreasing with increase in composition up to x=0.075, and then increases.
2. Field emission scanning electron (FESEM) micrographs showed (i) Homogenous distribution of grains of sizes ranging from 1-2μm with clearly visible grain boundaries.(ii) The overall miscrostrucutre is densely packed, (iii) Average grain size decreases with increase in compositional .

3. The ferroelectric to paraelectric phase transition temperature was found to be 110^0C for pure PFN and decreases with increase concentration of $BaTiO_3$. Loss tangent is found to be increasing with increase of temperature.

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