Synthesis And Characterization of ferroelectric material $(Na_{0.5}Bi_{0.5})TiO_3$- Eu_2O_3 Ceramics

This thesis is submitted in partial fulfilment of the requirement for the degree of

Master of Science in

PHYSICS

by

KRISHNA KANT ODITYA

Under the supervision

of

Associate Prof. **S. Asthana**
Assistant Prof. **Manish K. Niranjan**

भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

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Krishnakant

(Signature)

(Krishna Kant Oditya)

PH14MSCST11008

(Roll No.)

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This thesis entitled **Synthesis and Characterization of Ferroelectric Material** by **Krishna Kant Oditya** is approved for the degree of Master of Science from IIT Hyderabad.

Vandana Sharma

Examiner

R. Bhuvanesh

Examiner

Dr. Saket Asthana

Adviser

Examiner

Examiner

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ABSTRACT

Lead free Na0.5Bi(0.5-x)EuxTiO3 ceramics were prepared by solid state reaction route taking five different composition with x=0.005,0.01,0.02,0.03,0.04 and 0.05 . From XRD pattern it is comfirmed that theNBT-Eu single phase were formed at differnt Eu_2O_3 doping. RAMAN pattern shows roughness or irregularity due to the data taken at high resolution . From morphological study by SEM it is found that the grains were well developed and have the dense structure. Also the grain shape changes from granular to plated with increase in concentreation of Eu_2O_3. From UV-VIS SPECTROSCOPY it is observed that the band gap increase with increase Eu_2O_3 concentration. The PE-LOOP analysis shows that the remnant polarization (Pr) and coercive field (E_c) values increase with increase in concentration. The dielectric constant increases with increase in tempreature also the broadening of the peaks is observed with increase in concentration.

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INTRODUCTION

Dielectric are basically electric insulators. In such materials electrons are very tightly bound to the atoms and the atoms and they do not conduct any electric current. In dielectrics the centers of positive and negative charges coincides. So no conductivity is possible. When a sufficient magnitude of electric field is applied to the crystal, centres of positive charges slightly displaced in the direction of field and the negative charges in opposite direction. This produces electric dipoles throughout the crystal. And the crystal is said to be polarized.

POLARIZATION

When a dielectric material is placed in an external electric field , it becomes polarized i.e. in a small volume of substance the geometrical sum of the electric dipole moment vectors of the molecules becomes nonzero.
The polarization “P” is expressed as the dipole moment per unit volume

$$\text{i.e. } P = p / v$$

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

$$P = N*p$$

Frequency Dependence of Dielectric Properties: Resonance

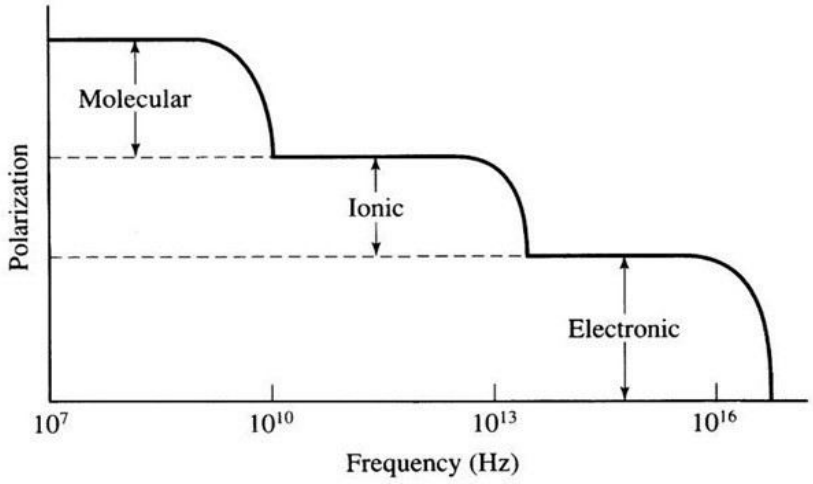
The electric polarizability of the atom is defined as the dipole moment per local electric field

$$\text{i.e. } \alpha = p/E_{loc}$$

Mechanisms of Polarization

Basically, there are four mechanisms of polarization:

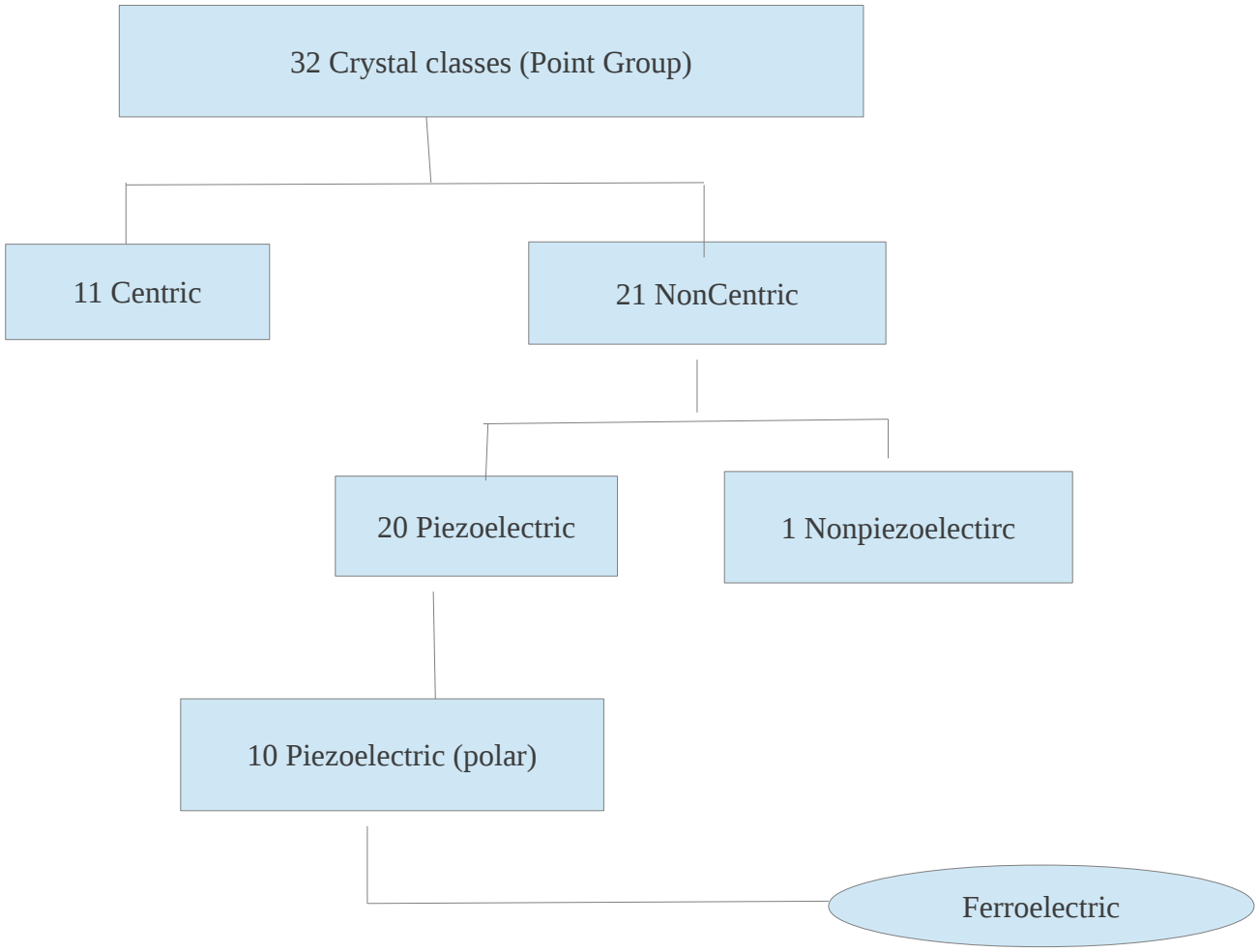
1. Electronics or Atomic Polarization
2. Ionic Polariztion
3. Dipolar or Orientation Polarization
4. Interface or space charge Polarization



Classification of symmetry Elements :-

There are 32 symmetry classes (point groups) out of which 21 point groups are noncentrosymmetric and 11 are having centre of symmetry . We are interested in these 21 groups as they posses dipoles.

Again out of 21, 20 groups show piezoelectric behaviour. Out of these 20 points groups, 10 point groups have unique polar axis and are exhibit pyroelectric effect. These 10 divided into ferroelectrics and nonferroelctrics.



PIEZOELECTRICITY

Piezoelectricity forces applied to a segment of material lead to the appearence of electrical charge of the surface of the segment.

In schematic one dimensional notation , the piezoelctric equation are :-

$$P=Z\,d + \varepsilon_0 E\,\chi \qquad \text{.....(i)}$$

$$e=Zs+Ed \qquad \text{.....(ii)}$$

Where, P represents polarization , Z the stress , d the piezoelectric strain constant, E the electric field , χ the dielectric susceptibillity ,

e the elastic strain and s the elastic compliance constant.

Equation (i) exhibits the devlopment of polarization by an applied stress. And equation (ii) shows the development of elastic strain by applied electric field.

The absence of centre of inversion is the prerequisite for the occurance of piezoelectricity materials are used to convert electrical energy to mechanical energy to mechanical energy and vice versa. They are used in devices such as Microphones , strain gauge , ultrasonic generators etc.

Ferroelectricity

A ferroelectric material is like a ferromagnetic one exhibits spontaneous polariazation even in the absence of an externl electric field . The spontaneous polarization gets destroyed and the ferroelectricity disappears above a certain temperature called the transition temperature (or the Curie tempreature) where the materials become paraelectric.

The occurrence of ferroelectricity may be understood in terms of either :-

i) Polarization catastrophe

ii) Transverse optical phonon mode.

The inernal electric dipoles of a ferroelectric material are physically tied to the material lattice so anything that changes the physically lattice will change the strength of the dipoles and cause a current to flow into or out of the capacitor even without the presence of an external voltage across the capacitor.

Two stimuli that will change the lattice dimension of material are force and tempreature . The generation of a current in response to the application of a force to capactior is called piezoelectricity.

Introduction to NBT :-

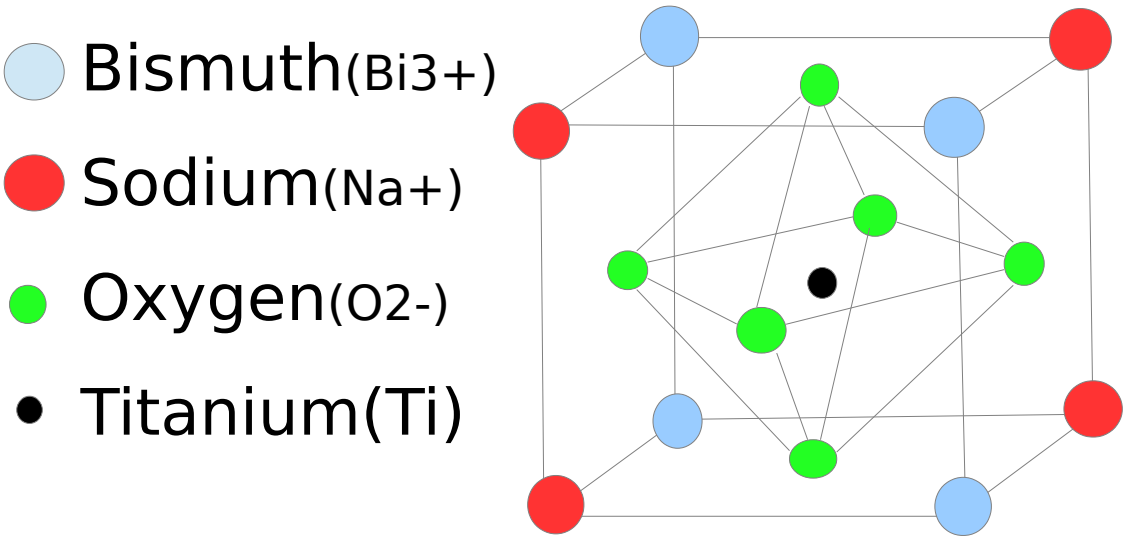
Lead based piezoelectric ceramics with pervoskite structure based on Lead zirconate Titanate (PZT) are widely used for sensors, actuators as well as microelectronic device because of their excellent piezoelectric properties due to existence of Morphological Phase Boundary (MPB). Because of the high toxicity of lead oxide, the use of the leadbase ceramics has caused serious lead pollution and enviromental problems. Therefore it is necessary to devlope lead free piezoelectric ceramics for replacing them.

Sodium bismuth titanate is a dielectric material which is being used widley due to its high temperature dielectric constant and it is a lead free material complex having Bi3+ and Na+ on the A-site of ABO3 pervoskite structure with a rhombohedral symmetry. It is considered as one of the good candidates for leadfree piezoelectric ceramics because of a large remnant polarization at room tempreature.

Structure of Sodium Bismuth Titanate:-

Sodium bismuth titanate is an ABO_3 disorted pervoskite with an rhombohedral R3c crystal structure at room tempreature . The standard ABO_3 pervoskite formula for NBT is ($Na_{0.5}Bi_{0.5}TiO_3$) . An ABO_3 pervoskite can be considered in two ways; one way occupy the corners of a cubic unit cell, oxygen cations occupying the face centeres, and a titanium cation in the face centres of the oxygen octhedra that is formed.

The other way, a three dimensional cubic network of 8-corner sharing TiO_6 Octahedra with bismuth and sodium cations as the centre of the cubic formed by the octahedral.



CHAPTER 2

THESIS OBJECTIVE

To prepare the different composition of NBT & Europium by using the formula (Na0.5Bi(0.5-x)EuxTiO2)

2.1 Litreature Review :-

The NBT material was discovered in 1960 by Smolenskii et.al. In 1990, by various sources the optical and dielectric properties of NBT were reported by park et al., [1-3] . The existence fo rhombohedral symmetry at room tempreature was found out by Jones and Thomas in 2002. When heated, structural transition take place from tetragonal to cubic.

Polycrystalline of Leadfree sodium bismtuh titanate (NBT) ferroelectrics ceramics doped with rare earth (RE) element are prepared using solid state reaction method . Optical ferroelectric and electrocaloric properties were investigated. The introduction fo RE 3+ ions in the NBT host lattice shows different light emissions over the wavelength range from visible to near infrared region.

The of P-E hysterisis loop exhibits an antiferroelectric like character near room temperature indicating possible existences of a morphotroic phase boundary . The enhanced electrocaloric response was observed in a broad temperature transition Coexsistence of Optical and electrocaloric properties is very promising for photn- ics or optoelectronic device application.

R.K. Prusty et al. Investigated Eu doped $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) shows a pleteauing of emission intensity beyond 12% Bi substitution. This occurs at the same doping concentration at which modulus is restored to pure NBT values.This simultaneous effect can be explained using a nanophase segregation model. Nano indentation and spectroscopy based result suggest suggest that the solide state solubility or Eu in $Na_{0.5}Bi_{(0.5-x)}TiO_3$ corresponds to $0.05 \leq x \leq 0.06$.

The most efficient emitter among the segregated phase is the Eu saturated NBT phase, which is the primary contrinutor to the lumiscence. Here one expects platrauing of PL intensity beyond X=0.06,The phase segregation model is supportedby spectroscopic evidence; ie. , They obtain strong Raman signal of Rule NBT at x=0.06 . The precise physico- chemical origins of the decrease in modulus with respect to dillute Eu doping merits further investigation . This may perhaps provide an understanding of the decrease in d33 coefficients in RE doped pervoskite system (when compared to the parent pervoskite.

CHAPTER 3

This chapter includes the details about synthesis of NBT-Eu ceramics and different experimental techniques used to characterize it

EXPERIMENTAL TECHNIQUES

(A) Preparation of solid of NBT-Eu by solid state reaction route.

(B) Characterization of the different composition of NBT- Eu ceramics.

SYNTHESIS METHOD

(A) Powder preaparation

(B) Ball milling

(c) Powder calcination

(D) Pelletization

(E) Sintering of pellets

CHARACTERIZATION TECHNIQUES

(A) X- ray differaction

(B) Raman spectroscopy

(C) Scanning Electron Micoscopy

(D) uv-visible Spectroscop

(E) Dielectric study

(F) P-E loop

The raw material used ofr synthesis of NBT-EU :-

Sodium Carbonate (Na_2CO_3)

Bismuth oxide (Bi_2O_3)

Europium (i i i) oxide (Eu_2O_3)

Titanium dioxide (TiO_2)

The chemical equation of NBT-Eu :-

$$Na_2CO_3 + Bi_2O_3 + (x)Eu_2O_3 + TiO_2 \longrightarrow 4(Na_{0.5}Bi_{(0.5-x)}Eu_xTiO_3) + CO_2$$

Powder preparation by solid state reaction synthesis :-

Solid state synthesis method was adopted to produce power $Na0.5Bi_{(0.5-x)}Eu_xTiO_3$ was prepared with x=0 , 0.005 ,0.01 , 0.02 ,0.03 , 0.04 , 0.05 . For powder preparation bismuth . For powder preapation byismuth oxide (Bi_2O_3) powder, sodium carbonate (Na_2CO_3) powder, titanium dioxide (TiO_2) , Europium(iii) oxide (Eu_2O_3) was used. The powders were weighted and mixed properly in a mortor. After mixing in dry condition isopropyl alcohal was added and mixed and againgrind - -ing was done till it bacame dry.

Calcination of Powder :-

The powder was grinding and dried properly and then calcined in alumina crucible at 1073 k for 3 hours . The calcination help in driving out all volatile and gaseous material from powder.

Compaction into Pellets :-

The calcined powder was mixed with 3% PVA solution (for binding) . It was mixed in an agate mortor and left to dry. After drying it was scraped and grounded to time powder . The different composition powder were separetly packed agter being weighted (around 0.5gm) . The powder was then pressed into pellet by unaxial compaction with load or 4 ton.

Sintering of Pellets :-

The cacined powders of different were sintered at 1100 (degree) C in a furnance for four hours. Sinterning is done to density the pellets and to make compact. The sinterning also cause the diffusion of atoms which will help in grain growth and the decrease in porosit is also observed. The type of furnance used is an electrically heated one. To get good result it is necessary to control the heating rate and tempreature.

Explanation of different Chaacterization Techniques :-

X-Ray diffraction (XRD) :-

X-Rays are electromagnetic radiation having shorter wavelength than of visible light . X-ray diffractometer based on the principle bragg' s law which is given by

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

Where , d is the spacing between the atomic planes.

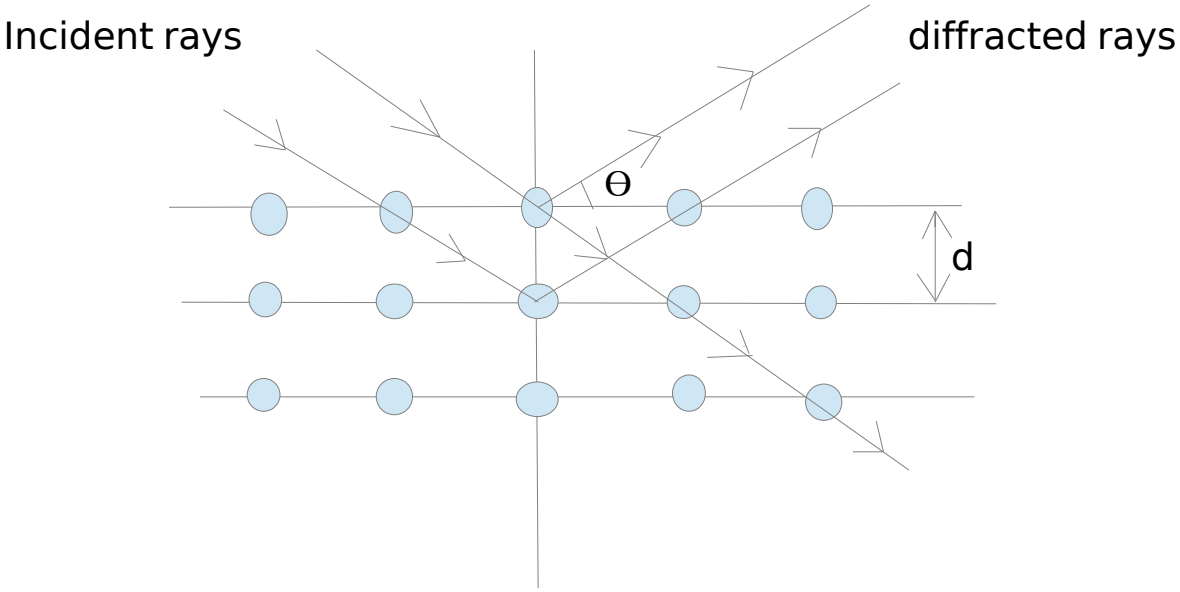
λ is the wavelength of X-Ray used

Θ is the angle of differaction ,

And n=1,2,3

The X-rays diffraction a techniques for determination fo different phase present in the sample, crystal structure and the Crystallite size

The pellets of different composition of sodium bismuth titanate and lithium niobate were subjected to X-ray diffraction and the results were obtained.



Scanning Electron Microscopy (SEM) :-

In SEM when a beam of high energetic electrons strikes the sample x-rays , secondary electron , and back scattered electron are produced from the sample. The detector the collects these electronics and converted into signal and displays on the screen. Since layer of platinum is coated using a sputter coater. Generally SEM provides the inforrmation about the surfaces of the specimen and it can't scan deep into surface. In SEM the electrons beam are focused beam are focused on small area of the sample . This charac--terization technique provides the information about the surface morphology of the sintered pellets.

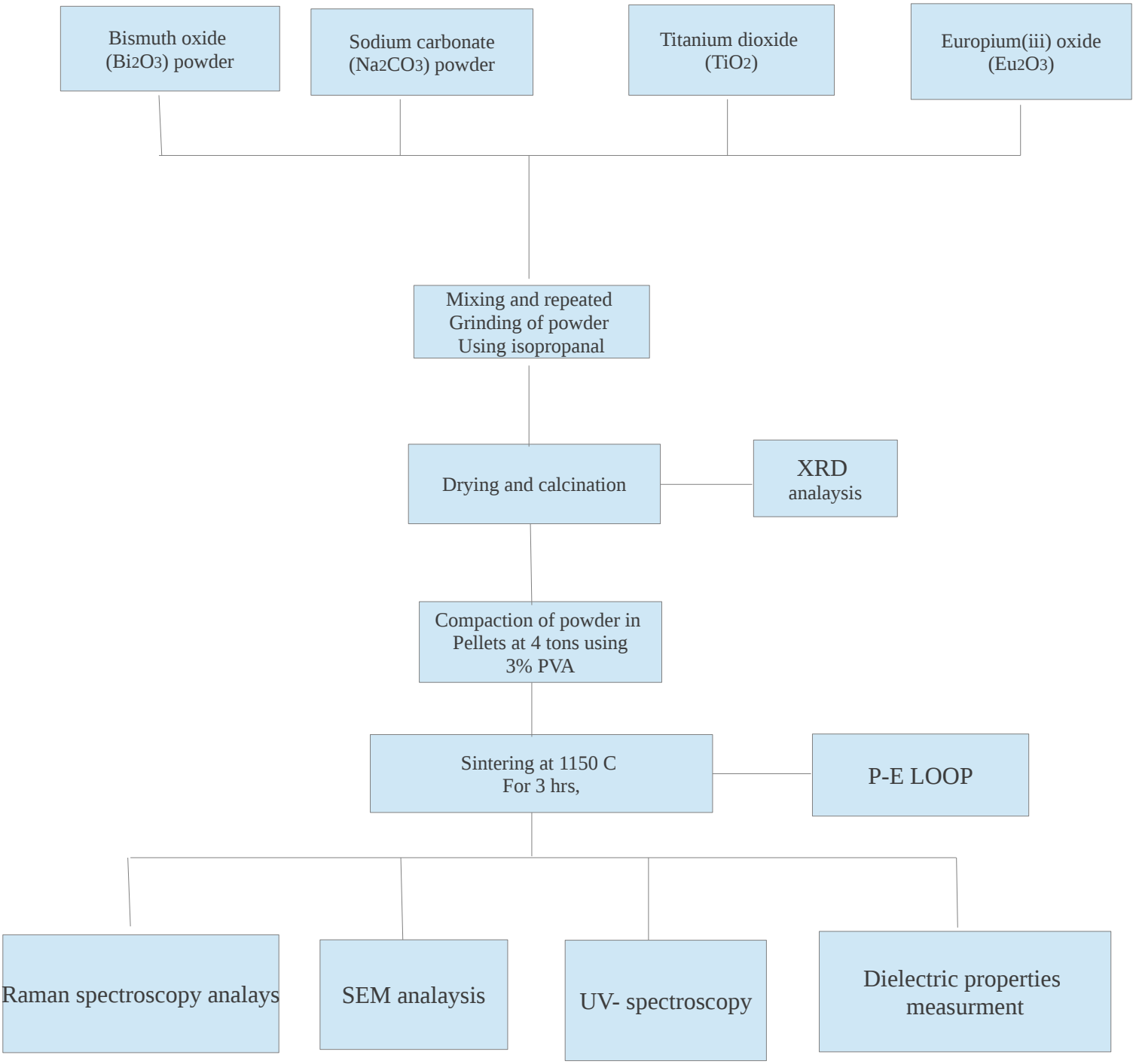
Dielectric study :-

For dielectric measurment the impeadance analyzer was used. The data containing phase, impeadence capacitance and conductance are collected are collected as a function as a function of frequencies at different tempreatures.

Raman Spectroscopy study :-

Raman spectroscopy is a technique by which we can analyze the vibrational and rotational modes in a system.The frequency in raman lines are not determined by the scattered but by the incident frequency.

Flow chart of the procedure for prepartion of NBT-Eu :-

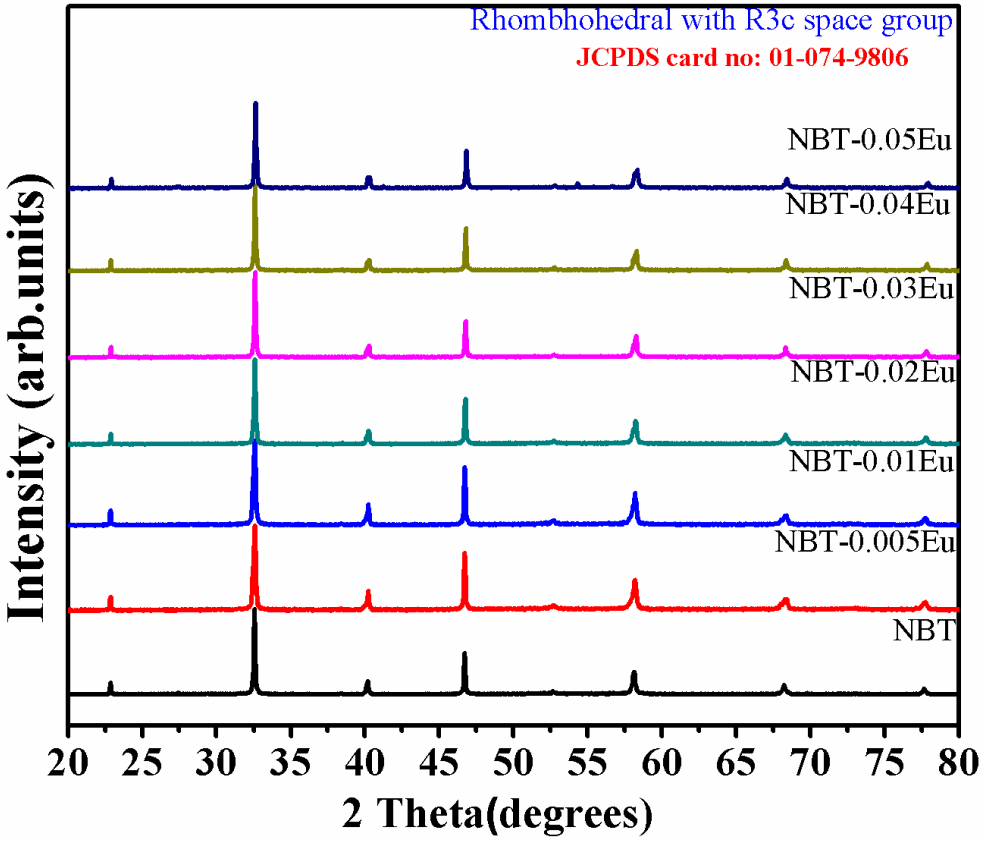


Chapter 4

RESULT AND DISCUSSION :-

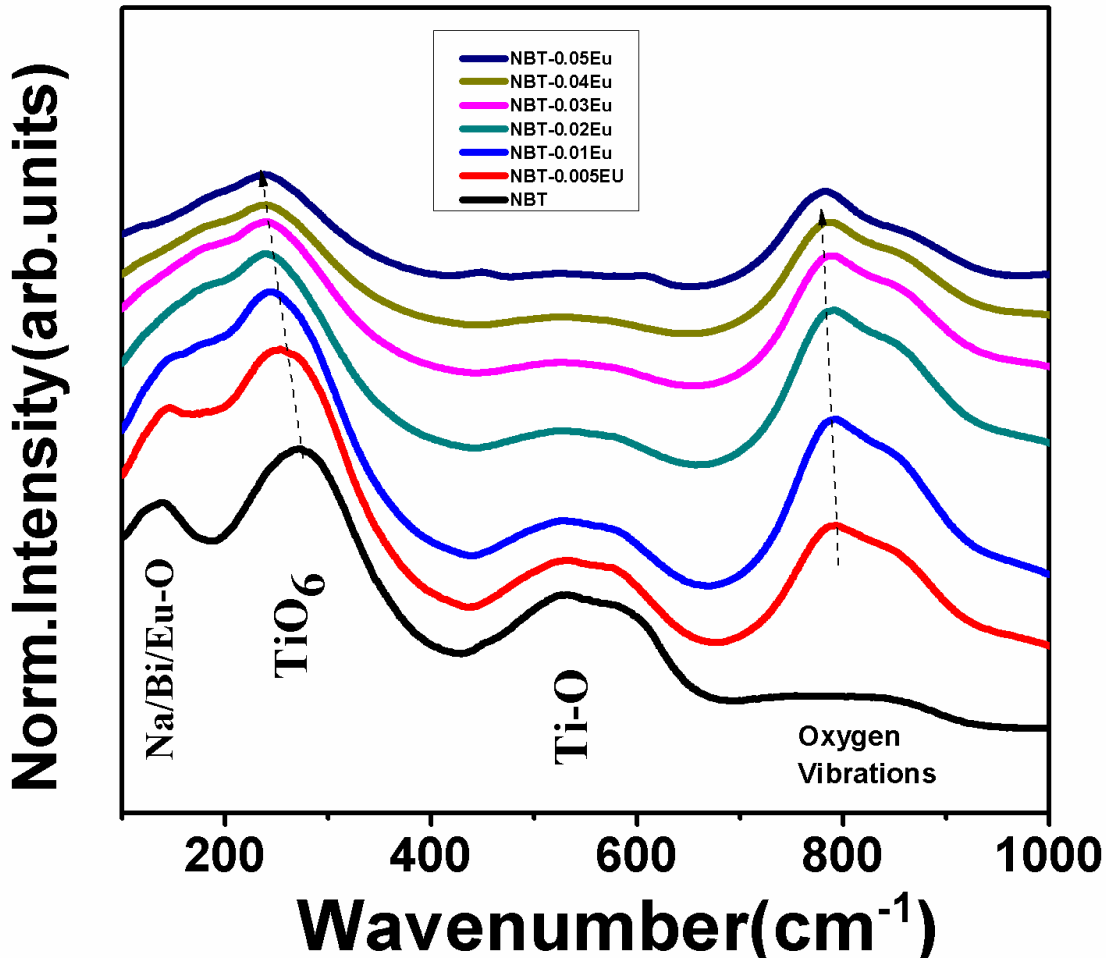
1. XRD ANALAYSIS :-

Fig . 1 shows the XRD pattern of ($Na_{0.5}Bi_{(0.5-x)}Eu_xTiO_3$) ceramics with various x values at room tempreature . The XRD peaks of the NBT and the NBT-Eu ceramics were in agreement with those of the previous NBT phase with the ABO_3 pervoskite structure. This indicated that observed. Thus , the NBT-Eu ceramics, as well as the NBT ceramics, had a rohmbohedral system. The position of peaks shifted towards lower angle at higher concentreation of Eu may be due to sudden rise of strain in the material by the solubility limit of Eu in the NBT lattice were reached.



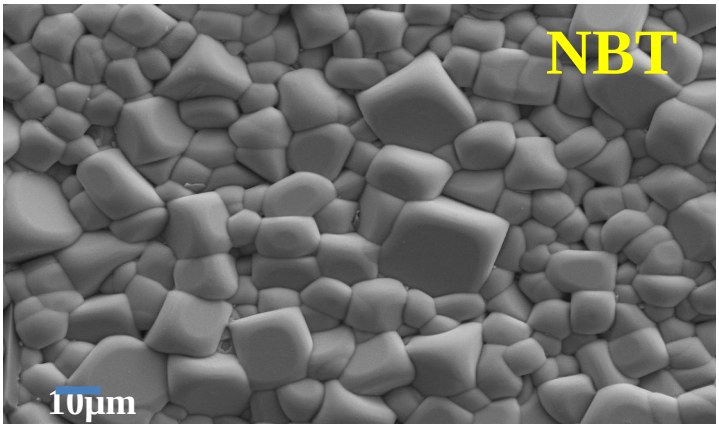
2. Raman Spectroscopy :-

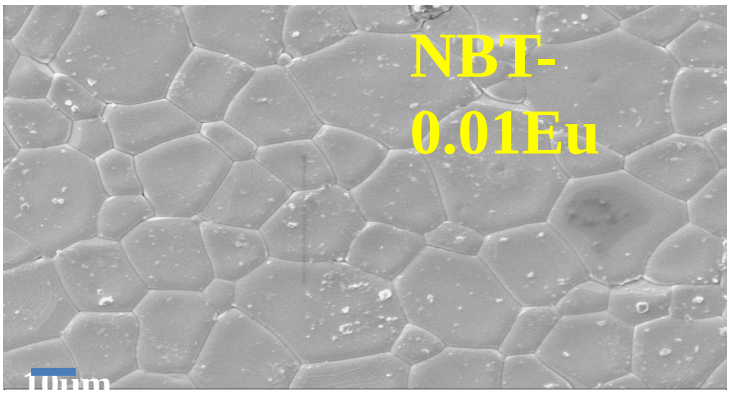
As per the group theory analysis , NBT (rohmbohedral,R3c) should show 13 Raman active modes ; in irreducible representation $\Gamma_{Raman} = 7A1+6E$ . . Therfore, among the 13 Raman-active vibrational modes it is possible to observe 8 Raman-active from fitting deconvolution of the Raman spectrum of NBTand all the compostion of NBT-Eu ceramics (only Lorenzation Area function) . This can be attributed to A-site and B-site disorder and the overlapping of Raman modes due to the lattice anharmonicity . The Raman patterns shows roughness or irregularity due to the data taken in high resolution , it makes noise while collection or data . If we take the data taken the data in high resolution, then it is impossible to distinsguish the closely bounded molecules.

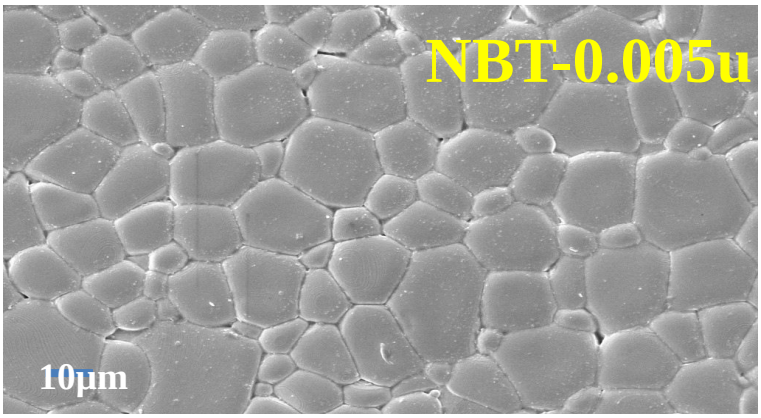


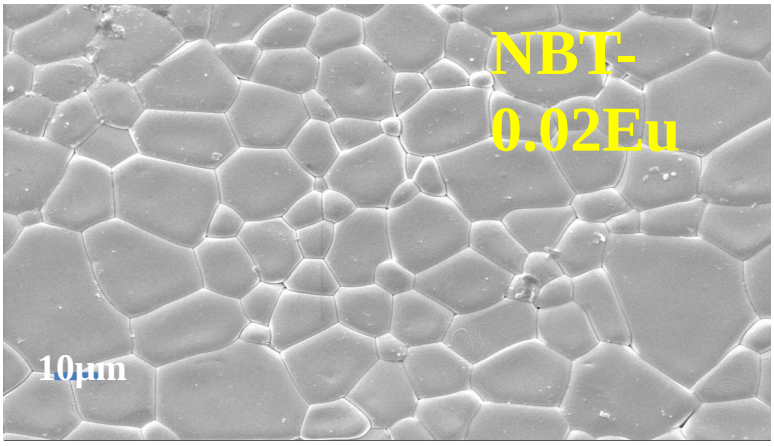
3. Scanning Electron Microscopy Analysis :-

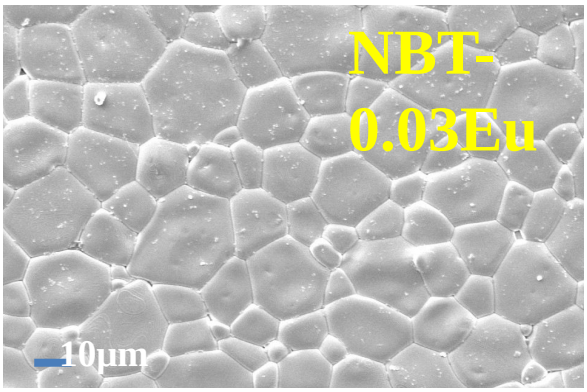
Fig .3 shows SEM images of the pure NBT and the NBT-Eu ceramics. The grains were well developed at sintering tempreatures of 1075- 1150 (degree) C for 4 hrs. The grains of the NBTceramics had a dense structure, which were similar to those of a typical NBTceramics. With incre-asing Eu_2O_3 , the grain shape changed from granular-like grains for NBT to plated grains plated grains for NBT-Eu ceramics. Grain growth is slightly inhibited after Eu_2O_3 doping for ceramics $(Na_{0.5}Bi_{(0.5-x)}TiO_3)$ ceramic system and thus non-uniform grains are formed.

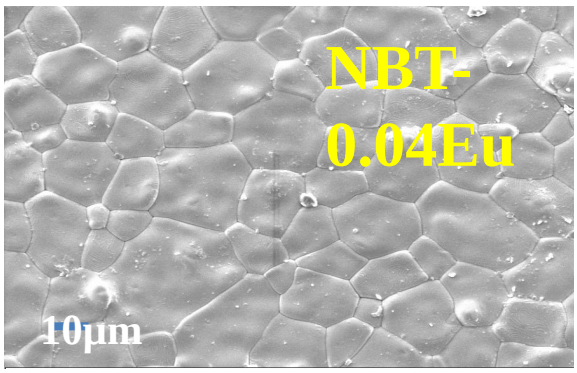












4. UV Visible Spectroscopy Analaysis :-

The opticle band gape energy (E_{gap}) was estimated for NBT-Eu ceramics by using the method proposed by Wood and Taue and presented in Fig. . According to these authors the optical band gap is associated with the absorbance and photon energy by the following equation :

$$h\nu a \quad \alpha\ (h\nu - E_{gap})n$$

Where h is the Plank constant , a is the absorbance, v is the frequency, E_{gap} is the optical band gap n is a constant associated to the different types of electronic transition (n=0.5,2,1.5 or 3) for direct allowed, indirect allowed, direct forbidden and indirect forbidden transition, respectively). In our work, the UV-visible absorbance spectra indicated an indirect allowed transition and , therefore the value of n=2 are used in the above equation. The litreature describes that the band gap energy is indirect when the electronic transitions occur from maximum-energy states located near or in the valence band (VB) to minimum energy states below or in the conduction band (CB), but in different regions in the Brillouin zone. Thus, the E_{gap} value for NBT-Eu powders was evaluated extrapolating the linear portion of the curve or tail. The enhanced optical band gap is observed with the increase in LN content in NBT-Eu ceramics in the studied composition range.

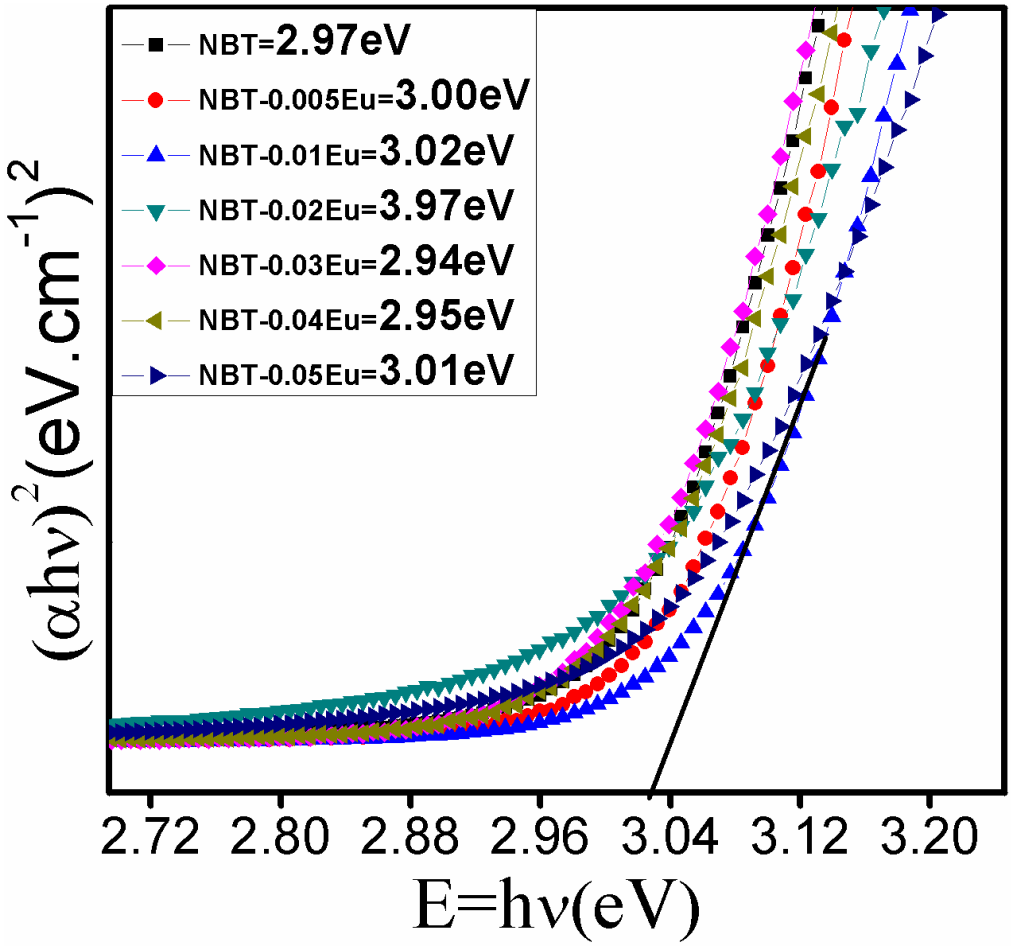


Fig. : The Opticle band gap calculated by extrapolating the linear portion of the absorption spectra for NBT-Eu ceramics.

In principle, this behaviour indicates the existance of different intermediary energy levels within the band gap of these materials, which can be arising from the structural order – disorder into the lattice. Thus, the increase of Eu content is able to induce a structural rearrangment, reducing the presence of these energy levels within the band gap and increasing the E_{gap} values. Based on this hypothesis, we believe that the intermediary energy levles are composed of deep and shallows holes.

5. P-E LOOP :-

Fig. Shows the P-E hystersis loops of the NBTand NBT-Eu ceramics at room tempreature . It can be seen that typical ferroelectric polarization hysteresis loops were obtained for all samples under an electric of 35 kV/cm at15Hz. It is found that the Eu content has an effect on the ferroelectric properties of the ceramics . It can be seen that Pr and Ec values generally increase with increasing the Eu content. P-E loops not very slim probably because of slightly high leakage currents as can be seen form the round angle of the P-E loops at the maximum elctric field and at the higher concentration of Eu content.

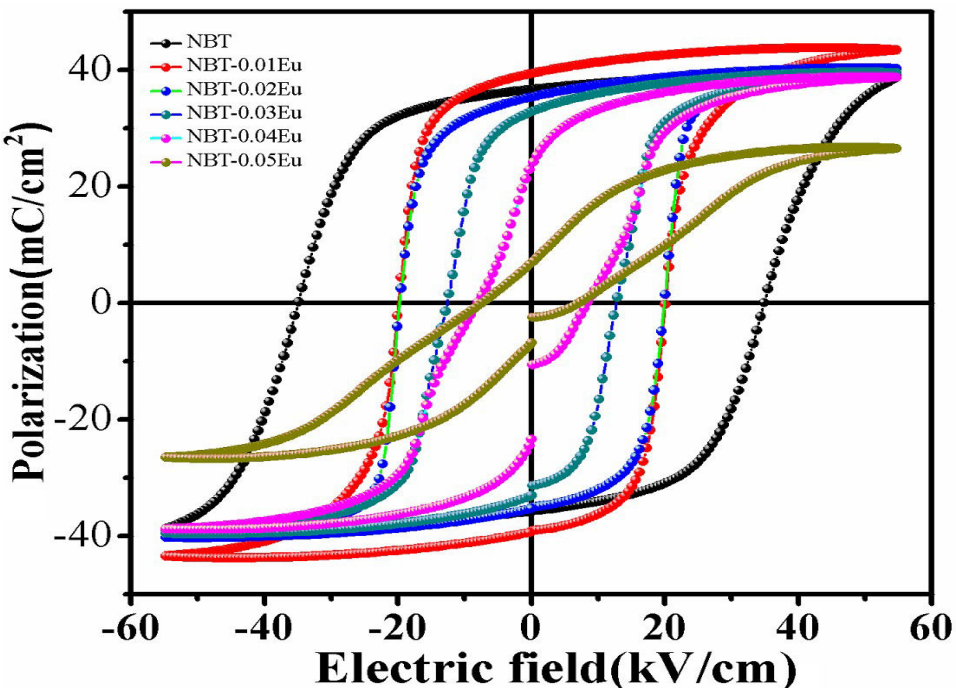
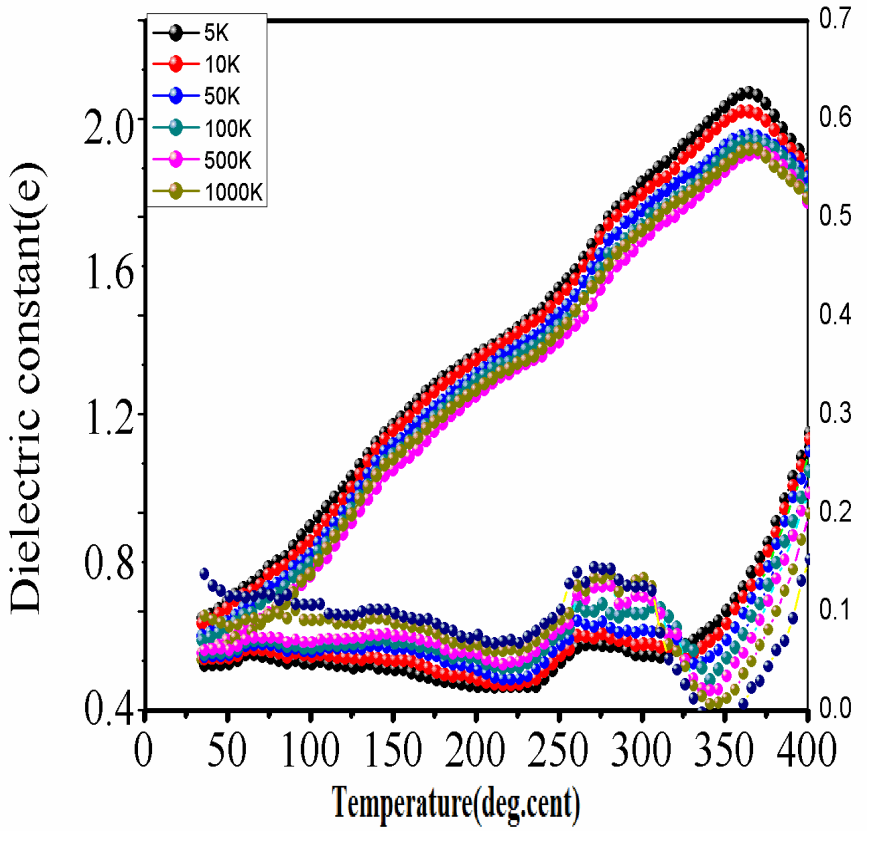


Fig: Ferroelectric P-E loops of the NBTand the NBT-Eu ceramics.

6. DIELECTRIC STUDY :-

Fig. Shows the tempreature dependence of releative premittivity at a frequency of 100 kHz. There are two dielectric peaks for the NBTceramic . The first peak in around 200*C is the dipolarization tempreature (T_d), which is similar to that of the phase transition to the ferroelectric to the antiferroelectric phase. The second peak is a phase transition to the paraelectric phase. The variation in the dielectric behaviours are at tributed to the increased Eu_2O_3 doping. With increasing Eu_2O_3 doping, the dielectric peak near T_m= 350*C broandened and shifted to low tempreature.The dielectric properties with a broad dielectric maximum are reported to be due to the contribution of a realxor behaviour, which is called a diffuse phase tranistion (DPT). In this work, Eu_2O_3 doping caused an inhomogeneous



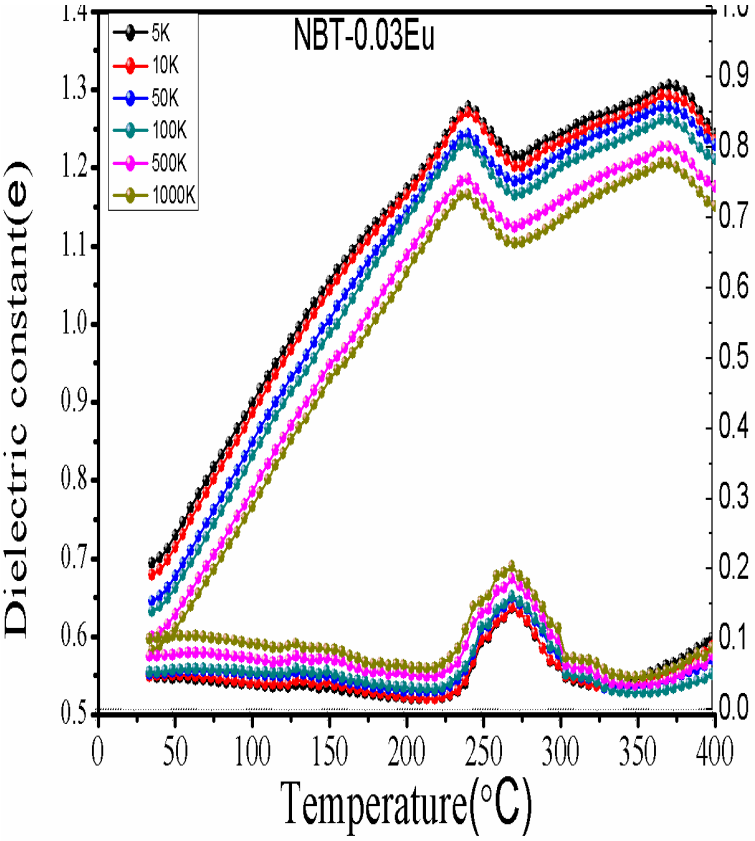


Fig. Dielectric constant to the NBT-Eu 0.01, 0.02 ceramic system.

composition and a more disordered crystal structure, That results the broad maximum. Thus, the diffuse phase transition could be explained by the coexistence of a (Na,Bi,Eu) ion at the B-site .

Fig. Shows the tempreature dependence of dielectric loss (tanΘ) at a frequency of 100kHz. With increasing tempreature, the dielectric constant of the NBTceramics decreased tempreature of 300*C and then increased due to bismuth and oxygen vacancies are created at high sintering tempreature, which cause the low frequency dielectric dispersion and high conductivity. The defects get trapped at sites like grain electrode and grain boundary interfaces and results space charge polarization so electrical conductivity decreased. This implised that Eu_2O_3 doping reduces the contribution of space charge or ionic charge carriers.

CONCLUSION :-

Single phase Pervoskite NBT, Eu and $Na_{0.5}Bi_{(0.5-x)}Eu_xTiO_3$ ceramic successfully prepare through solid state reaction route.

XRD patterns indicating that the position of peaks shifted towards lower angle at higher concentration of Eu may be due to sudden rise of strain in the material.

The Raman patterns shows roughness or irregularity due to the data taken in high resolution.

SEM images shows that with increasing the Eu concentration the grain growth slightly inhibited and the grain shape changed from granular to plate shaped.

UV plot shows that the band gap increase with increase Eu concentration .

PE loop shows that the remnant polarization(Pr) and corecive field (E_c) increasing with increase in Eu concentration.

Dielectric study shows that with increasing Eu_2O_3 doping, the dielectric peak near T_m= 350 degree C broanded and shifted to low tempreature and the dielectric loss study shows the conductivity reduced due to increase in Eu concentration.

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