

# **The Effect of $Ba^{2+}$ on Strontium Bismuth Titanate**

**Aurivillius Structure**

*A thesis submitted in fragmentary fulfilment*

**FOR THE DEGREE OF MASTER OF SCIENCE IN PHYSICS**

**Under Academic Autonomy**

**NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA**

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**ROURKELA-769008, 2012-2013**



## NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

### CERTIFICATE

This is to certify that the thesis entitled, “*The effect of Ba<sup>2+</sup> on Strontium bismuth titanate Aurivillius structure*” submitted by *Ms Rashmi Rekha Negi* in partial fulfillments for the requirements for the award of Master of Science Degree in Physics Department at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

Place-Rourkela

Date:10.05.2013

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## **ABSTRACT**

*The ferroelectric material Strontium bismuth titanate ( $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ) and also the Ba doped SBT ( $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ ) was synthesized taking different concentration of Ba ( $x=0.04$  and  $0.1$ ) by solid state reaction method. The synthesized ceramics were then characterized with different characterization techniques. From XRD pattern the phase formation of the specimen was confirmed, SEM images showed the plate shaped grains and also the grain size increases with the increase in the concentration of the Ba content. P-E Loop confirms the ferroelectric property of the ceramic, the remnant polarization of the material decreases with the increase in the Ba content. From the UV-Vis Spectroscopy it was observed that the band gap energy of the material decreases with an increase in the concentration of the Ba content showing semiconducting behaviour and from the dielectric study it was observed that the dielectric constant of SBT at room temperature is 190. The transition temperature is above  $500^\circ\text{C}$  that is nearly  $520^\circ\text{C}$ . Also the dielectric loss was found to low and it decreases with an increase in the Ba content.*

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## CHAPTER 1

### INTRODUCTION

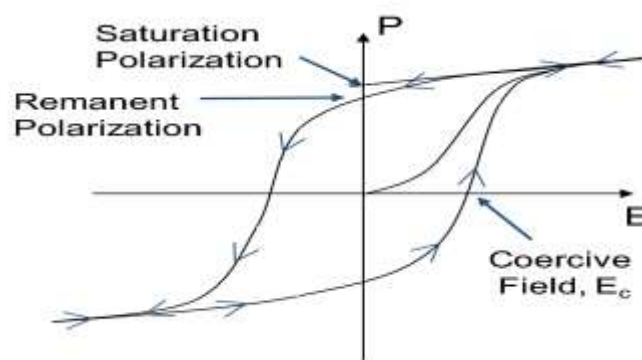
#### Ferroelectricity

Ferroelectricity is the phenomenon where spontaneous polarization of the material takes place i.e. polarization of the material takes place in the absence of an electric field. It is thus analogous to ferromagnetism which represents the state of spontaneous magnetization of the material. The materials exhibiting the phenomenon of ferroelectricity are called ferroelectric materials. In ferromagnetic materials, the centres of positive and negative charges do not coincide with each other even when there is no electric field, thus producing non-zero dipole moment. Valasek in 1921 first observed the ferroelectric effect in Rochelle salt. This has molecular formula  $\text{KNa}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ .

#### Properties of ferroelectricity

##### Hysteresis loop (P vs E)

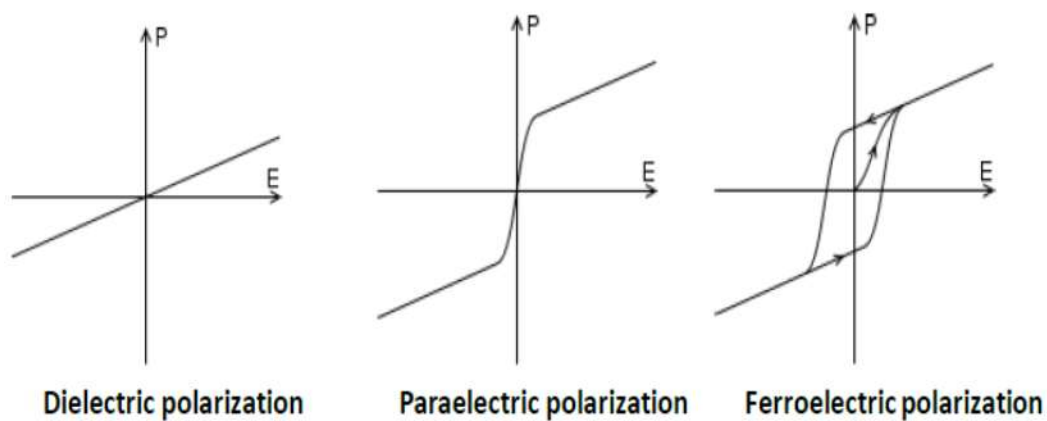
The plot of polarization vs. electric field in ferroelectric material is called hysteresis loop.



(Fig-1: P-E loop showing ferroelectric property)

P-E loop is the characteristic property of the ferroelectric materials. When a ferroelectric material is subjected to an electric field the material is polarised. At first the polarisation rises rapidly with the applied field and above this its behaviour becomes linear on application of field. If we extrapolate linearly to y-axis, that is when the field is zero, it gives the saturation or spontaneous polarisation. On reducing the field to zero, remnant polarisation is obtained. The negative field required to reduce the polarisation to zero is called as the coercive field. The hysteresis loop in ferromagnetic materials implies that there is a spontaneous polarisation in the material and depends upon the temperature. The shape of the hysteresis loop of a ferromagnetic substance changes on increasing the temperature. The height and width of the loop also changes with the increase in temperature. At a certain temperature all the ferroelectric behaviour of the material disappears and the hysteresis loop merges to a straight line called as the “ferroelectric curie temperature”.

All ferroelectric materials have a transition temperature called the Curie temperature ( $T_c$ ). At a temperature  $T > T_c$  the material does not exhibit ferroelectricity, while for  $T < T_c$  the material shows ferroelectricity. On decreasing the temperature through the Curie point, a ferroelectric material undergoes a phase transition from a non-ferroelectric phase to a ferroelectric phase. If more than one ferroelectric phase is present then the temperature at which the material transforms from one ferroelectric phase to another is known as transition temperature. The temperature dependence of the dielectric constant above Curie temperature ( $T < T_c$ ) in the ferromagnetic material is governed by the Curie-Weiss law  $\epsilon = C / (T - T_c)$ , where  $C$  and  $T_c$  are the Curie-Weiss constant and Curie-Weiss temperature respectively.



(Fig 2: P-E loop for different materials)

Most materials are polarized linearly with the application of the external electric field, nonlinearities are insignificant. This is called as dielectric polarization. Some materials called paraelectric materials shows nonlinear polarization. In addition to being non-linear, ferroelectric materials show a spontaneous polarization. Such materials are called pyroelectrics. The ferroelectrics have distinguishing feature i.e. the direction of the spontaneous polarization can be reversed by the application of electric field, giving a hysteresis loop. Typically, materials exhibit ferroelectricity only below a certain phase transition temperature, called the Curie temperature,  $T_c$ , and paraelectric above this temperature.



**ferroelectric materials are of two main groups :-****1. The order-disorder group:**

In the order-disorder group, the ferroelectric transition is associated with the individual ordering of ions.

Examples: Potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), Rubidium hydrogen phosphate ( $\text{RbH}_2\text{PO}_4$ ) etc.

**2. The displacive group:**

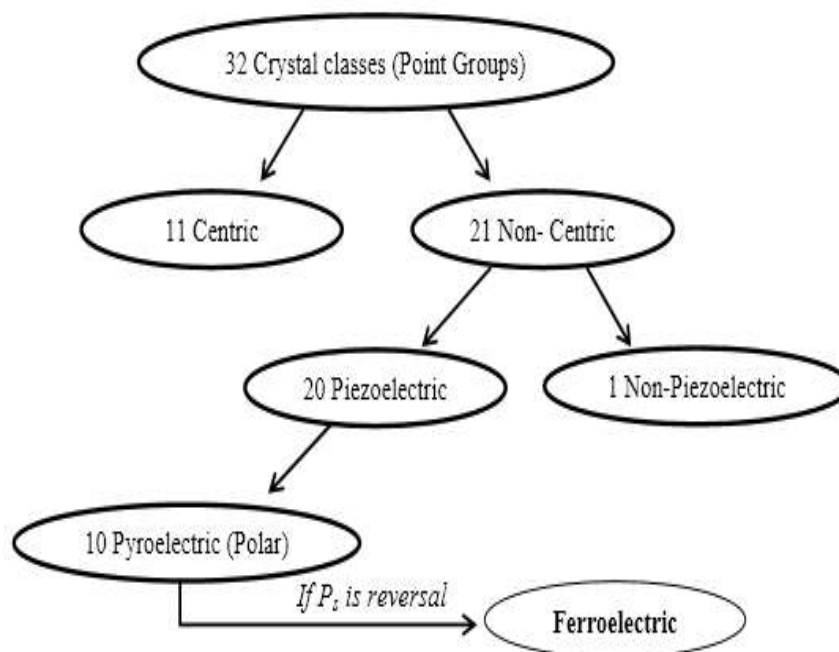
In displacive group of ferroelectrics the ferroelectric transition is associated with the displacement of a whole sublattice of ions of one type relative to a sublattice of another type.

Examples: Barium titanate ( $\text{BaTiO}_3$ ), Potassium niobate ( $\text{KNbO}_3$ )

**Basics of ferroelectric in Crystal**

Solid may be classified into:

1. **Amorphous**- The atoms are not arranged in a regular geometrical pattern. They are isotropic i.e. their properties are same in all directions. Examples are glass etc.
2. **Crystalline**- The atoms are arranged in a regular geometrical pattern and there is a smallest volume element which by repetition in 3D describes the crystal. This smallest element is called as a Unit cell.

codification of 32 crystallographic point groups

(fig -3: A classification scheme for the 32 crystallographic point groups)

Crystal can be divided into 32 crystal classes (point groups). Out of the 32 point groups, 11 are Centro symmetric and cannot exhibit polar properties. The remaining 21 are Non-centro symmetry and can possess one or more polar axes. Among 21 non-centro symmetry, 20 classes are piezoelectric and only one is Non-piezoelectric. Of the 20 piezoelectric classes, 10 have unique polar axis and thus exhibit spontaneous polarization. Crystals belonging to these 10 classes are called pyroelectric. Ferroelectric crystals belong to this family, but they also exhibit the additional property that when electric field is applied, the direction of spontaneous polarization can be reversed.

**Piezoelectricity**

When some materials are subjected to mechanical stress, electricity is produced. This is called the piezoelectric effect. This stress can be caused by hitting the material just enough to deform its crystal lattice without fracturing it called as the direct piezoelectric effect. Converse effect is also shown by piezoelectric materials, where deformation is produced on the application of a voltage, in tensor notation the direct and the converse piezoelectric effect is ,  
 $P = d_{ijk}\alpha_{jk}$  (direct piezoelectric effect)

$$\beta_{ij} = d_{ijk}E_k \text{ (converse piezoelectric effect)}$$

for direct piezoelectric effect,  $P$  is the polarization generated along  $i$ -axis due to the application of stress,  $d_{ijk}$  is the piezoelectric coefficient.

For converse piezoelectric effect,  $\beta_{ij}$  is the strain generated in the particular orientation of the crystal with the application of the electric field in the  $k$ -axis.

**Pyroelectricity**

When electricity is produced with the change in temperature, the phenomena is known as pyroelectricity. There are 10 pyroelectric crystals from among 21 non-centro symmetric crystals. Pyroelectricity is the ability of some materials to generate a temporary voltage when cooled or heated. The change in temperature modifies the position of atoms slightly within the crystal structure such that the polarization of the material changes as

$$\Delta P_s = \Pi \Delta T$$

$\Delta P_s$  = Spontaneous polarization

$\Pi$  = Pyroelectric coefficient

$\Delta T$  = Change in temperature

This means that spontaneous polarization depends upon temperature.

### **Applications of ferroelectric materials**

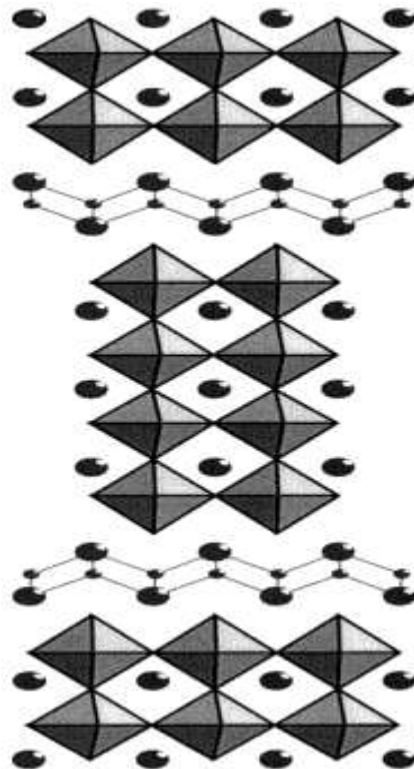
Ferroelectric materials are important for the manufacturing of capacitors, storage memories (ferroelectric random access memory), wave guides, optical memory display, displacement transducers.

### **Different types of ferroelectric structures**

There are four different types of ferroelectric structure and are-

1. Perovskite structure
2. Bismuth layer structure
3. Tungsten Bronze structure
4. Pyrochloro structure

### Bismuth Layer structure



( Fig -4: Bismuth layer structure (four layered) )

- The general formula of Aurivillius compounds is  $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{x-1}\text{B}_x\text{O}_{3x+1})^{2-}$  where 'A' represents 12 fold coordinated cation with low valences in the perovskite sublattice; B denotes the octahedral site with high valences; x is the number of octahedral layers in the perovskite block between the rock-salt type.
- The ferroelectrics materials with layered-structured is attractive from the view point of their application as electronic materials such as dielectrics, piezoelectrics and pyroelectrics, because they are characterized by good stability of piezoelectric properties, a high Curie temperature and a good resistance vs temperature.
- Some examples of Bi-layered structure are  $\text{SrBi}_2\text{Ti}_2\text{O}_9$ ,  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  etc.

**INTRODUCTION TO STRONTIUM BISMUTH TITANATE (SBT)**

- $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ (SBT) is an  $n = 4$  member of the Aurivillius family of layered perovskites (i.e bismuth layered perovskite structure).
- It is orthorhombic at room temperature, with a Curie temperature  $\sim 520^\circ\text{C}$ .
- SBT presents interest as lead-free high temperature piezoelectric with very high resistance to electrical fatigue during ferroelectric switching.
- This type of material exhibits good ferroelectric properties including moderate remnant polarization, low coercive field, long retention, and low tendency to imprint.
- Most important of all, layer-perovskite materials exhibit excellent fatigue endurance in comparison with PZT and its family.
- SBT has many advantages but the disadvantage is that it has low remnant polarization so to increase its remnant polarization; it is doped mostly with some rare earth elements.

**THESIS OBJECTIVE**

- To synthesize the four layered Aurivillius ferroelectric material Strontium bismuth titanate ( $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ) doped with Ba at Sr site by conventional solid state method.
- To characterize the synthesized material by XRD for phase analysis, SEM for surface morphology, PE-Loop to study the ferroelectric property of the material (like the remnant polarization, coercive field etc.), dielectric study to obtain the dielectric constant of the material, tangent loss etc. and optical characterization such as UV-VIS Spectroscopy to measure the band gap of the material.

### LITERATURE REVIEW

The bismuth layer-structured ferroelectrics have a crystal structure containing interleaved bismuth oxide  $(\text{Bi}_2\text{O}_2)^{2+}$  layers and pseudo-perovskite blocks which contains  $\text{BO}_6$  octahedral and generally formulated as  $(\text{Bi}_2\text{O}_2)^{2+} (\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ . Here A represents a mono, bi or trivalent ion, B corresponds to a tetra, penta or hexavalent ion, and m denotes the number of  $\text{BO}_6$  octahedral in each pseudo-perovskite block (m=1 to 5) [1].

The physical properties of this ceramic are strongly affected by the structure and morphology [2] currently Sr-based layered perovskite is one of the most promising candidates for a new generation of non-volatile ferroelectric random access memories (NvFRAM) devices [3].

Among several BLSF materials,  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  (SBT) is extensively studied by many researchers from possible applications in piezoelectric device [4].

Recently, much attention has been paid to SBT due to its high Curie temperature, large and stable  $2\text{Pr}$  after up to  $10^{11}$  cycles, and anisotropic physical properties [5].

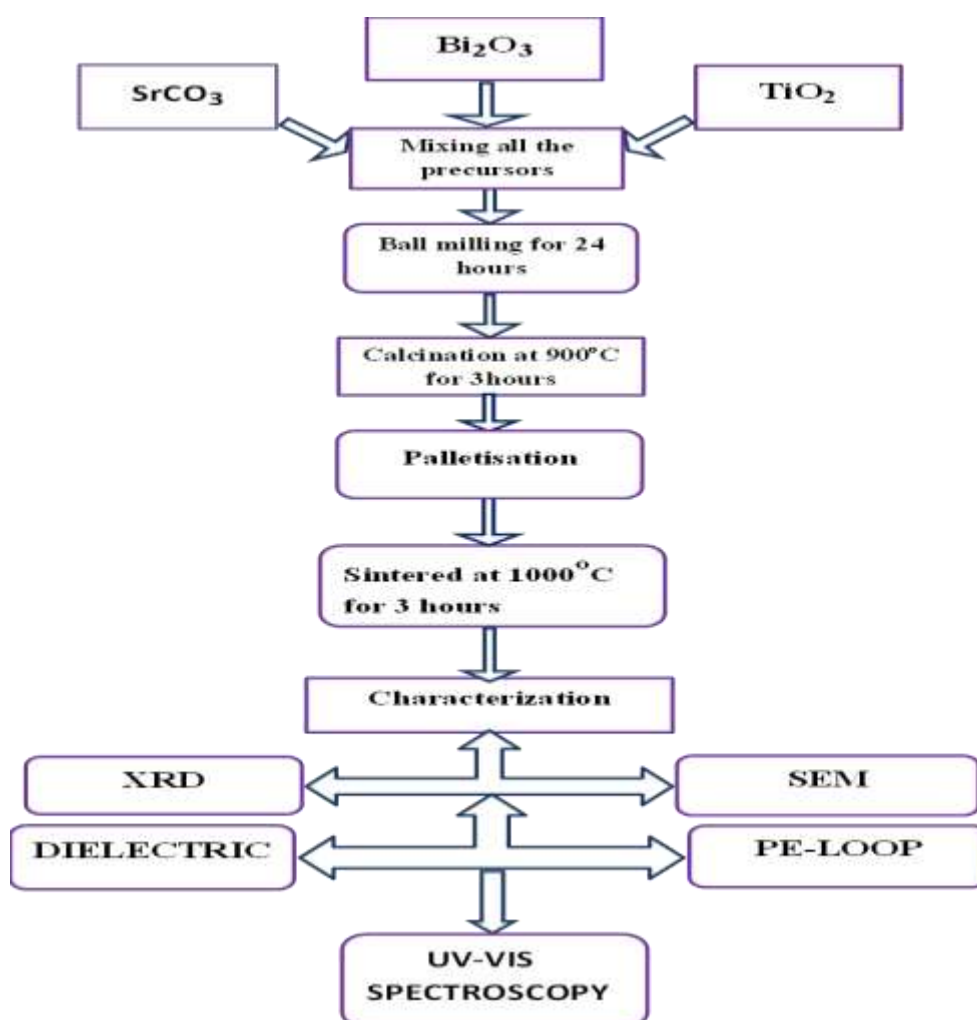
Because of its properties and performances, SBT is prepared by various methods [6].

The layered-structural ferroelectrics have recently attracted considerable attention for their application in low-voltage, high-speed ferroelectric memory because of good fatigue endurance [7].



**CHAPTER-3****EXPERIMENTAL TECHNIQUE**

In this chapter the details of the synthesis of the ceramic ferroelectric Strontium bismuth titanate ( $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ) with Ba doped is given in detail. And also the experimental techniques to characterize the specimen are briefly discussed.

**FLOW CHART FOR THE SYNTHESIS OF CERAMIC ( $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ )**

(Fig-5: Flow chart of synthesis of  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ )

The Ba doped ( $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ ) ceramic were prepared by solid state reaction method by taking raw materials such as (i) Strontium carbonate ( $\text{SrCO}_3$ ), (ii) Barium carbonate ( $\text{BaCO}_3$ ), (iii) Bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) (iv) Titanium dioxide ( $\text{TiO}_2$ ). Combining all the four precursors the ceramic compound ( $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ ) was formed, where x is the Ba concentration in the ceramic compound (x=0.00, 0.04, 0.10). The constituents of the required specimen were taken in a stoichiometric ratio. The mixing was accomplished in an agate motor and the pestle. Then the ceramics were ball milled for 24 hours to mix the powders properly in acetone medium using Zirconia balls. After ball milling the mixed powders were kept inside an electric furnace at  $900^\circ\text{C}$  for 3 hours for calcination.

After calcination, the pellets were made by mixing the powder with the binder (PVA) and giving hydraulic press for 4 mins. The pellets were then sintered in the electric furnace at  $1000^\circ\text{C}$  for 3 hours. Now the synthesized material was kept for XRD, SEM, UV-VIS Spectroscopy, P-E Loop and Dielectric study. For electrical study, silver paste has been used for the electrode of both sides of the sample.

The various steps in the solid state reaction method are represented by a flow chart as shown in the figure.

## **SYNTHESIS METHODS**

To prepare ceramic materials, the following synthesizing tools are used

### **Ball milling**

Ball milling is a method for grinding the material into fine powder. Ball mill rotates around a horizontal axis, partially filled with materials to be ground and the grinding medium such as zirconia balls. The material reduces to fine powder due to an internal cascading effect. The difference in speeds between the balls and grinding jars produces an interaction between

frictional and impact forces, which releases high forced energies. The interaction between these forces produces the high and very effective degree of size reduction of the planetary ball mill.

### **Calcination**

Calcination is a heat treatment process. In calcination solid state reaction takes place between the constituents particles of the material. And the volatile constituents like  $\text{CO}_2$ ,  $\text{SO}_2$ , moisture evaporates out. So the phase formation of the material takes place. But calcination takes place below melting point.

### **Pellet formation**

The calcined powders of different compositions mixed by PVA binder and grinded for four hours continuously. After drying the sample is scrapped out from the agate mortar and separately pellets are prepared by the help of die set and pelletize under a load of 5 ton.

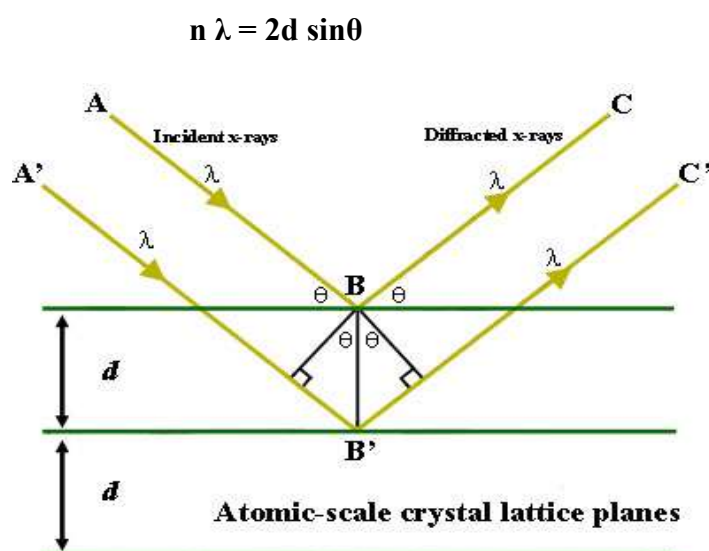
### **Sintering**

Sintering is also an heat treatment process. Basically it is based on atomic diffusion. Atomic diffusion takes place in any material above absolute zero, but faster at higher temperature. A simple example of sintering is that when ice cubes in a glass of water adhere to each other. The pore in the material collapses to densify the material.

## CHARACTERIZATION TECHNIQUES

### X-RAY DIFFRACTION

XRD is an analytical and most common technique for the study of crystal structure and atomic spacing. It is also used for the identification of phase of a crystalline material and also provides information on unit cell dimensions. XRD is based on the principle of interference. X-ray diffraction occurs when there is a constructive interference between the monochromatic x-rays and the crystalline sample. It follows Bragg's law and is given by-



(Fig-6: Principle of X-ray diffraction)

X-ray diffractometer gives a plot of intensity of diffracted beam as a function of the angle  $2\theta$ . The X-ray diffraction technique is a versatile method used to determine the phases, lattice defects, crystal structure, lattice strain and the crystallite size with a great accuracy.

### **SECONDARY ELECTRON MICROSCOPE (SEM)**

The SEM is a useful technique to study the topographical, morphological and composition of the materials with much higher resolution. When a beam of highly energetic electrons strikes the sample, the secondary electrons, X-rays and the back-scattered electrons are ejected from the sample. These electrons which are coming out of the sample are then collected by the detector and converted into signal that is displayed on the screen.

If the samples are non-conducting, a thin layer of platinum coat is given by using a sputter coater.

### **UV-VIS SPECTROSCOPY**

The UV-VIS Spectroscopy deals with the recording of absorption of light in the visible and UV regions of the spectrum. When radiant energy impinges upon a solution it may be absorbed, transmitted, reflected. In spectrophotometer the absorbed light is determined. However, because of the difficulty of directly measuring the absorbed energy, the transmitted energy is measured and the amount absorbed is indirectly determined by subtracting the transmitted from the initial energy.

### **PE-LOOP**

The PE-Loop of a material shows its ferroelectric property. It shows the variation of the polarization w.r.t to the applied electric field. It gives the values of the Remnant polarization ( $P_r$ ) and the Coercive field ( $E_C$ ). It also gives the value of saturation polarization ( $P_S$ ).

## **DIELECTRIC MEASUREMENT**

To measure the relative permittivity (dielectric constant) and dielectric loss, LCR meter can be used. The electrode samples were used to take the measurements. The LCR meter, was connected with the computer and the data (capacitance and D factor) was collected as a function of temperature at different frequencies. The capacitance measured was then converted using the following formula:

$$C = \epsilon_0 \epsilon_r A / d$$

Where, C: capacitance in farad

$\epsilon_0$  = permittivity in free space in farad/meter

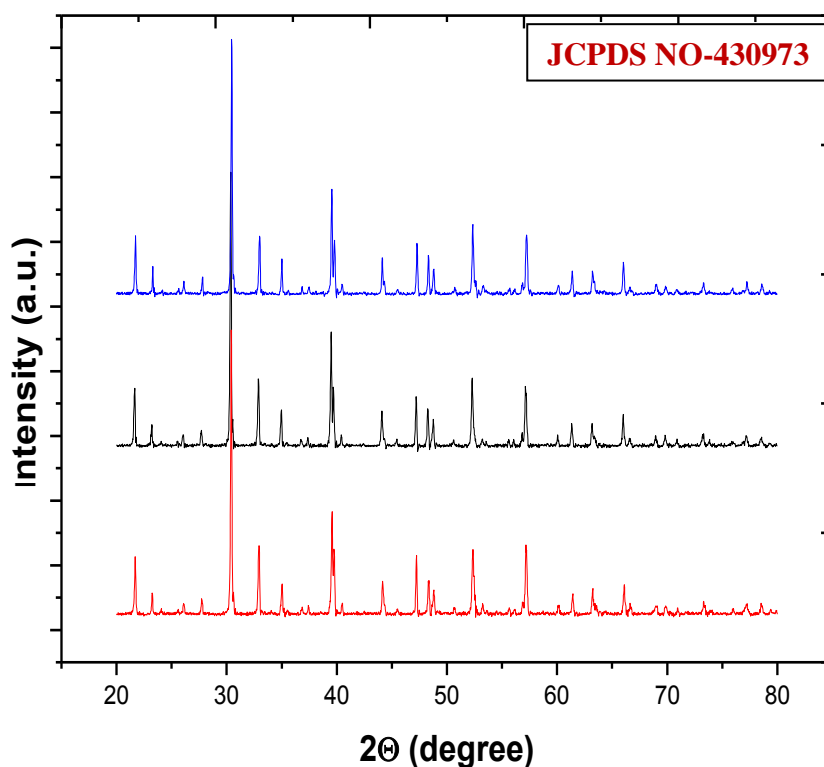
$\epsilon_r$  = relative permittivity of the sample

A = area of each electrode in m<sup>2</sup>

d = distance between the two electrodes in m

**CHAPTER-4****RESULT AND DISCUSSION****1. XRD ANALYSIS**

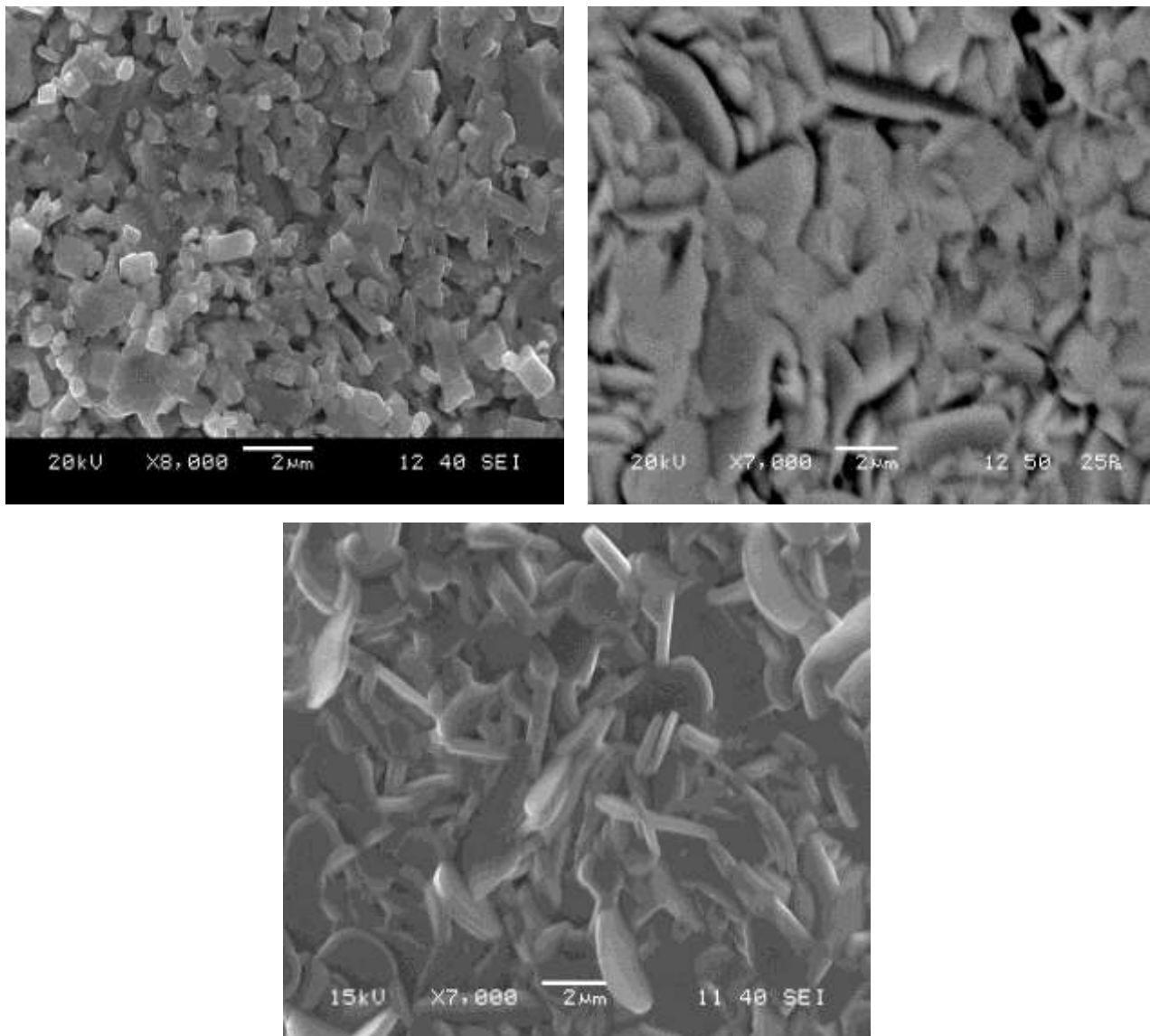
The SrBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> ceramics were prepared by solid state reaction method. The XRD pattern of SBT and Ba doped SBT (Sr<sub>1-x</sub>Ba<sub>x</sub>Bi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>) ceramic powders calcined at 900<sup>o</sup>C for 3 hours is shown in the figure. According to JCPDS no- 430973, all the peaks in the pattern are matching and it is showing orthorhombic single phase crystal. The lattice parameters are found to be, a=5.4507, b=5.4376, c=40.9841. As the concentration of Ba content in Sr increases, the peaks in the pattern shift towards right (increase in the 2 $\Theta$  position), which shows the shift in 2 $\Theta$  position clearly. This shift is obvious because of the substitution of larger ionic size Ba<sup>2+</sup> (1.34A) in place of smaller ionic size Sr<sup>2+</sup> (1.19A).



(Fig.7-XRD patterns of Sr<sub>1-x</sub>Ba<sub>x</sub>Bi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> ceramics)

## 2. SEM ANALYSIS

The figure shows the surface morphology of the parent material (SBT) and Ba doped SBT (Ba-0.04, 0.1). From the SEM images it is seen that the grains are plate shaped, homogeneously distributed. It is also seen that the ceramics are densified. With the increasing concentration of Ba content, the grain size increases.

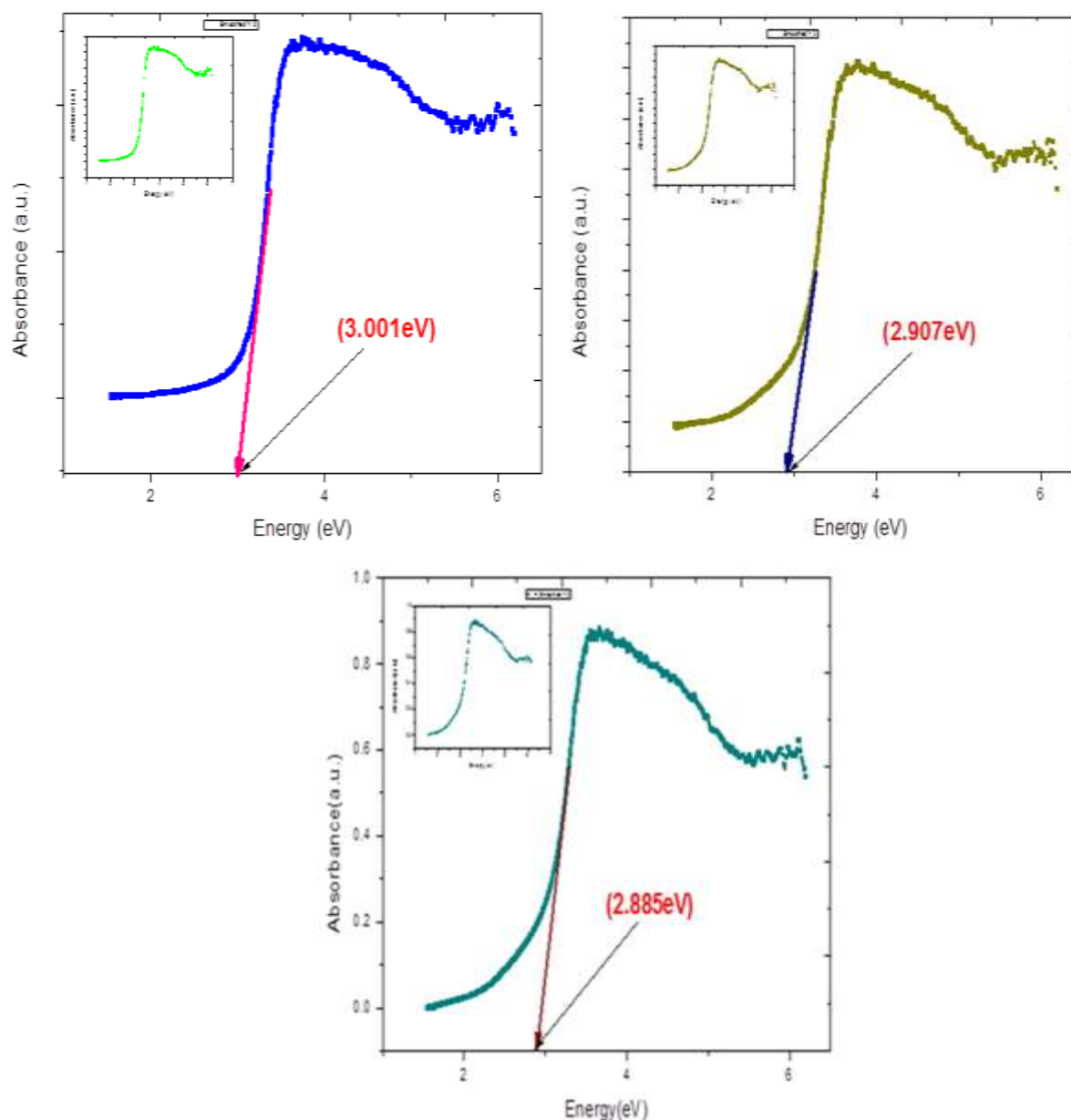


(Fig.8- Scanning electron microscopy (SEM) of Sr<sub>1-x</sub>Ba<sub>x</sub>Bi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> ceramics)



### 3. UV-VIS SPECTROSCOPY

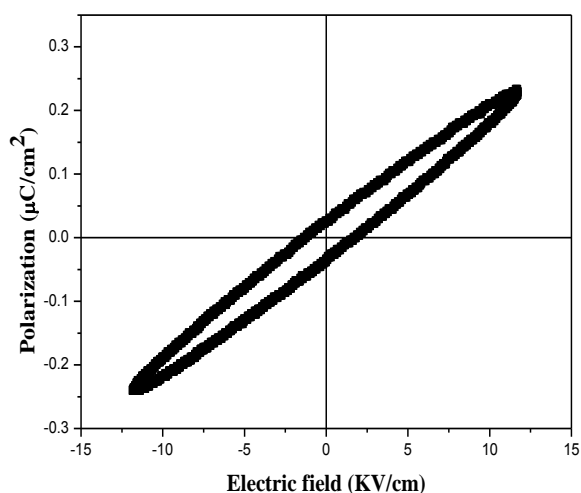
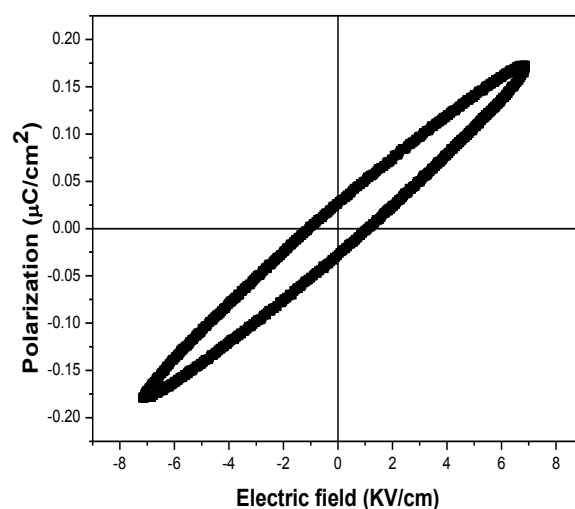
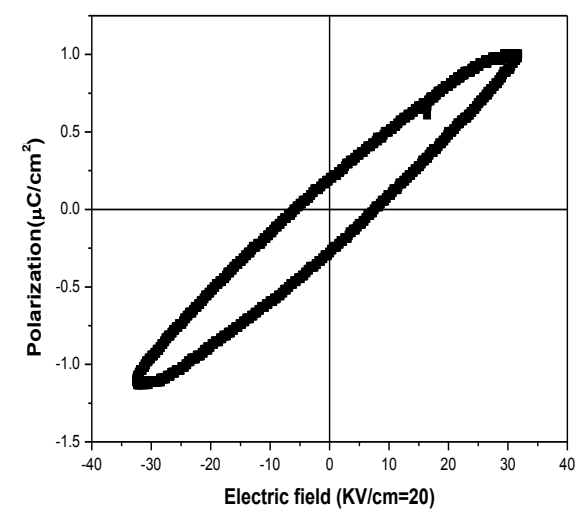
From the UV-VIS Spectroscopy for SBT and Ba doped SBT, it was observed that the band gap energy of the material decreases with an decreases with an increase in the Ba concentration which shows the semiconducting behavior.



(Fig.9- The optical band gap calculated by extrapolating the linear portion of the absorption spectra for Sr<sub>1-x</sub>Ba<sub>x</sub>Bi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> ceramics).

**4. PE-LOOP**

From the PE-Loop for the parent SBT and Ba doped SBT as shown in the figure below, it is observed that the Remnant polarization decreases with an increase in the Ba concentration in SBT.

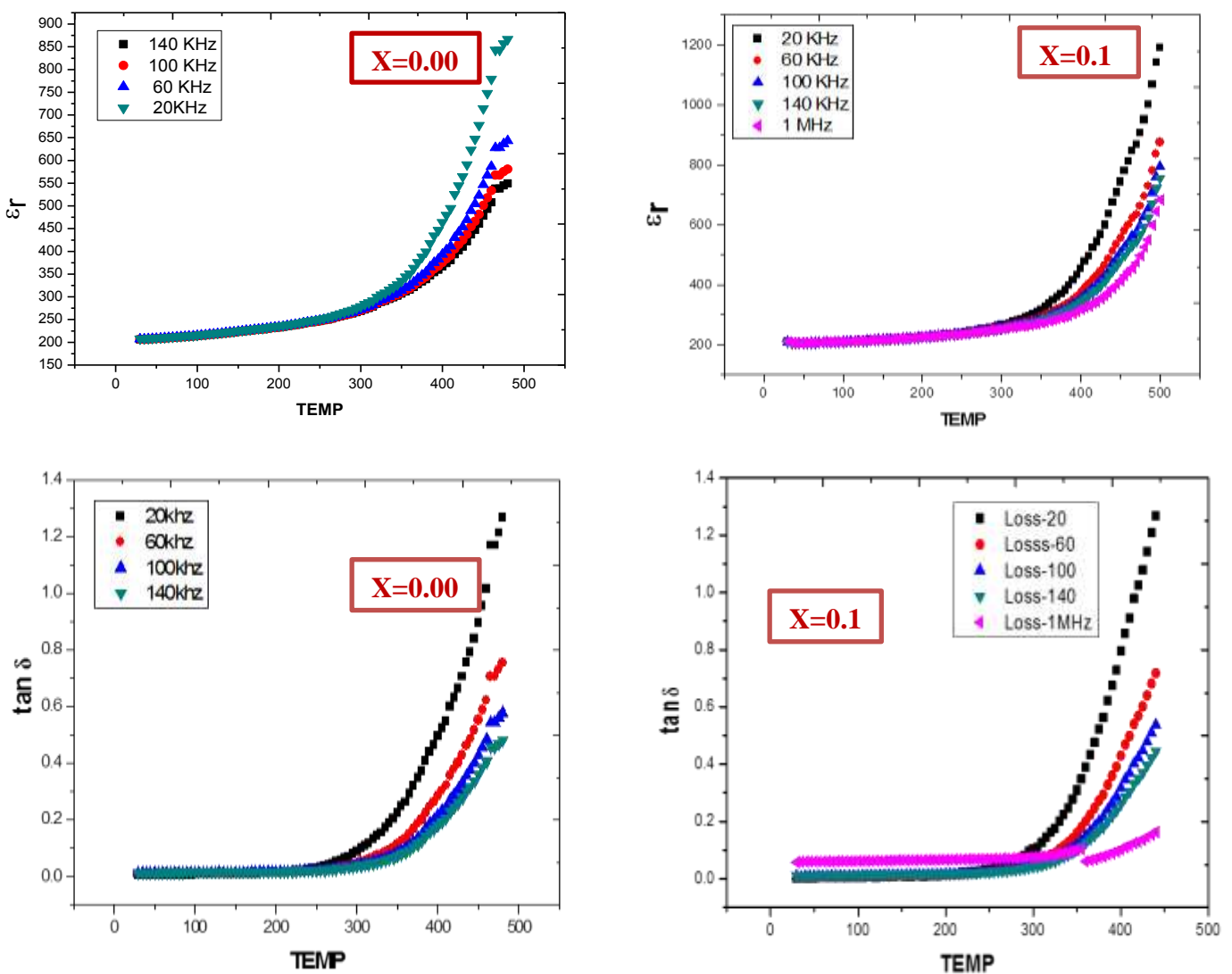


Sample	Remnant polarization ( $P_r$ ) in $\mu\text{C}/\text{cm}^2$	Coercive field ( $E_c$ ) in KV/cm
SBT	0.189	-5.54
Ba doped SBT (0.04)	0.025	-1.0025
Ba doped SBT (0.1)	0.0248	-1.2491

(Fig.10- Ferroelectric P-E hysteresis loops of the  $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$  ceramics).

**5. DIELECTRIC STUDY**

From the Dielectric study it was observed that the  $T_c$  of the material (SBT) is around  $190^\circ\text{C}$  at room temperature. Also from the figure below it is seen that the  $T_c$  of the material is above  $500^\circ\text{C}$  and from the literature review it was found that the  $T_c$  is nearly about  $520^\circ\text{C}$ . from the  $\tan\delta$  vs. temp. graph it is observed that the loss is less and decreases with an decreases with an increasing Ba content in SBT.



(Fig.11-Dielectric constant and Dielectric loss of the  $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_4\text{Ti}_4$  Ceramics at different frequencies).

**CHAPTER-5****CONCLUSION**

- Ba doped SBT was synthesized by Solid state method.
- X-ray diffraction confirms the single phase formation.
- Plate shaped grains were observed from SEM micrograph.
- PE-Loop confirmed that Remnant polarization gradually decreases with the increasing Ba concentration.
- From UV-VIS Spectroscopy it was observed that the band gap energy decreases with the increasing Ba concentration which is approaching towards semiconductor range.
- From the dielectric study it was found that the dielectric constant of SBT at room temperature is 190 at 1 MHz frequency and the dielectric loss is less and decreases with the increasing Ba concentration.

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