Synthesis and characterizations of $(Bi_{0.5}Na_{0.5})TiO_3$-$CaTiO_3$ceramic system

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By

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CERTIFICATE

This is to certify that the thesis entitled "**Synthesis and characterization of $Bi_{0.5}Na_{0.5}TiO_3 - CaTiO_3$ ceramic powders"** submitted by SunitaBehera in partial fulfillments for the requirements for the award of the degree in Master of Science in Physics, National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in this project has not been submitted to any other University/ Institute for the award of any degree in M.Sc Physics.

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15.05.2012 SUNITA BEHERA

DEDICATED

TO

MY PARENTS

ABSTRACT

Lead free $(1-x)(Bi_{0.5}Na_{0.5})TiO_3–xCaTiO_3$ ceramics were prepared by solid state reaction route taking five different compositions with x = 0.01, 0.03, 0.05, 0.07 and 0.09. Perovskite-like single-phase compounds were confirmed from X-ray diffraction analysis. Also the X-ray diffraction analysis confirmed that with the increase in the concentration of CT, the lattice parameter decreases. The Raman spectroscopy study confirmed that, the lattice parameters changed, which well aligned with XRD study. Surface morphology was successfully studied from SEM image which conformed that the grain size and shape changed with increasing CT concentration. Dielectric measurements conformed that, T_c increases, dielectric constant decreases and dielectric loss increases with increase in wt% of CT.

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CHAPTER - 1

INTRODUCTION

Dielectrics are the special type of insulators which do not have free electric charge carriersbut on the application of a strong electric field they get polarized.

Polarization means the development of dipoles by the application of anelectric field. Polarizations are categorized into different types:

a) Electronic polarization

b) Ionic polarization

c) Orientation / Dipolar polarization

d) Space charge polarization

Electronic polarization

When a neutral atom is subjected to an oscillating electric field, the electron cloud sweeps accordingly.This causes the shifting of charge centres which resultsin the formation of dipole moment. This is known as electronic polarization.

Ionic Polarization

The relative displacement of ions in an ionic solid when subjected to an oscillating field is referred asan ionic polarization. It occurs in ionic solids.

Both electronic and ionic polarizations are intra-atomic phenomena, showing resonance effect and are temperature independent.

Orientation/Dipolar polarization

In the absence of an electric field there is random orientation of dipoles. But on the application of electric field the dipoles getaligned and are polarized.

Space charge polarization

The charges which escapes from the metallic interfaces to the sample and mostly the free charge carriers trapped in vacancies respond to the applied field by sweeping accordingly. This is known as space charge polarization

Both the dipolar and space charge polarization are inter atomic polarizations andaremostly temperature dependant.

1.1 Ferroelectricity

The phenomena by which the materials possesses spontaneous polarization even if the external field is removed from the specimen is called as ferroelectricity and the materials showing this type of behavior are called asferroelectric materials [1].

PE loop is a typical property of the ferroelectric material. In ferroelectric materials the polarization does not alignwith the electric field. This phenomenonwas discovered in the year 1920 by Valasek[2].

Applications of ferroelectric materials: The ferroelectric materials have wide applications in optoelectronics and photonics due to their change in optical property. They are also used as

Capacitors, Oscillators and filters, Light deflector, modulators and displays, non volatile memory etc [3].

1.2 Sodium bismuth titanate

The Sodium bismuth titanate is a lead free ferroelectric material which was first discovered by Smolenskiiin 1960 [4].The ionsi.e$Bi^{3+}$and Na^{+}occupy the A-site and the titanium is present at the centre. The symmetry considered in this compound is rhombohedral [5]. Because of having very high temperature dielectric constant it is being very widely used.TheBNT ceramics exhibit weak ferroelectric property and are difficult to polarize.

1.3 Structure of sodium bismuth titanate:

Sodium Bismuth titanate is aABO_3 type of perovskite structure with rhombohedral R3c crystal structure at room temperature [6]. In this perovskite structure,the bismuth cations occupy the corners of a cubic unit cell and the sodium cations occupy the face centres while the titanium occupy the centre of cubic unit cell.

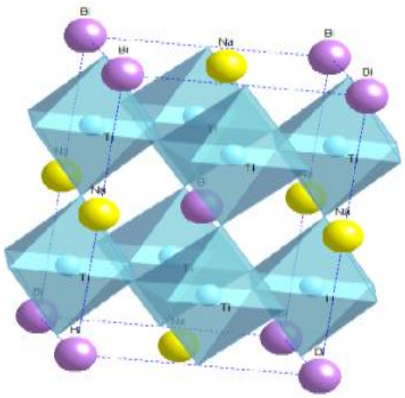


Fig. 1 Structure of BNT

CHAPTER-2

2. Thesis objective

a) To prepare different compositions of BNT and CT by using the formula (1-x) BNT-xCT.

b) To study the effect on BNT by adding different compositions of CT by performing different characterizations.

2.1 Literature review

The BNT material was first reported in 1960 by Smolenskiiet.al. In 1990, by various sources the optical and dielectric properties of BNT were reported [7-9]. The existence of rhombohedral symmetry at room temperature was found out byJones and Thomas in 2002. When heated,structural transition takes place from tetragonal to cubic .These BNT materials are having high Curie temperature. It is a lead free ferroelectric material. Doping has to be done to improve the properties of BNT materials. Some of the few examples of doping are -

Doping of $Bi_{0.5}Na_{0.5}TiO_3$ -$CaTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$- $BaTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$-$PbTiO_3$,$Bi_{0.}Na_{0.5}TiO_3$ - $K_{0.5}B_{0.5}TiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$and $Bi_{0.5}Na_{0.5}TiO_3$ -$BiFeO_3$.

Y.Yuan et al. reported the dielectric property, ferroelectric property and microstructure of (1-x) BNT-x CT [10]. By the addition of Ca, the dielectric constant peak was broadened and depressed which showed the weakening of ferroelectric behavior and induction of the par electricbehavior leading to the shift in the depolarization temperature. Large amount of long grains were observed on the surface of pure BNCT12. The growth of the grains were inhibited and the grains were elongated and vanished with the addition of <=0.6wt% of Mn. But there was an abnormal grain growth and

again appearance of rectangular grains with the increase of Mn content to >= 0.9 wt%. On addition of 0.9 wt% of Mn, highest densities were observed.

RuzhongZuo et al. studied the influence of A-site non stoichiometry on sintering, microstructure and electrical properties of $Bi_{0.5}Na_{0.5}TiO_3$[11]. By using the process of conventional solid state route, lead free ceramic $(Bi_{0.5}Na_{0.5})_{1+x}$- TiO_3(with x= -0.02, -0.01, -0.005, 0, 0.005, 0.01) were prepared. The properties like densification, microstructure, dielectric and piezoelectric were studied. It was found that with the excess amount of cation in the A- site the physical and chemical properties can be improved and the stoichiometry can also be controlled.

Jiaming Li et al. investigated the addition of Fe and La on the dielectric, ferroelectric and the piezoelectric properties of $(Bi_{0.5}Na_{0.5})TiO_3$– $Bi_{0.5}Li_{0.5}TiO_3$ – $BaTiO_3$ Mn ceramics. A hard effect was created with a coercive field E_c of 2.9 kv/mm with the doping of Fe [12].While doping of La produced a soft effect with the improvement in piezoelectric constant with the decrease in coercive field. A large strain value at the depolarization temperature was obtained which conformed the presence of short range order and the presence of non polar phases in the ferroelectric matrix. Wei-chih Lee et al. established the relation between morphotropic phase boundary composition and the tolerance factor "t" in $(Bi_{0.5}Na_{0.5})TiO_3$piezoelectric ceramics[13].The MPB compositions of t values were taken to be 0.990-0.993. Two piezoelectric systems (1 –x) $Bi_{0.5}Na_{0.5}TiO_3$ – x $(Ba_{1-a}Sr_a)$ with a=0.05 and 0.3 (BNBST5-x and BNBST30-x ,x<12%) were used .With X-ray diffraction analysis and its lattice parameter investigations the two systems were found to show the rhombohedral to tetragonal phase transformation. Measurement of structural and electrical properties revealed the MPB compositions of BNBST5-6 and BNBST30-8 with t value of 0.9900 and 0.9903 respectively which conformed the relation between MPB compositions and t value.

Nagata et al. reported on the properties of BNT by the addition of $BaTiO_3$ and BKT [14]. It was reported that at a composition containing 82.5% BNT,2.8% $BaTiO_3$ and 12% $Bi_{0.5}Na_{0.5}TiO_3$ morphotrophic phase boundary exists because of the anomalous electrical behavior associated with MPB compositions.

Man-Soon Yoon used the pre synthesized $BaTiO_3$ and pre milled bismuth oxide, sodium carbonate, and barium carbonate powders [15].The BNT – BT property was increased.

CHAPTER-3

This chapter deals with the details of the synthesis of BNT- CT ceramics and different experimental techniques employed to characterize it.

3.1 EXPERIMENTAL TECHNIQUE

a) Preparation of solidsolution of BNT-CT by solid state reaction synthesis route.

b) Characterization of different compositions of BNT – CT powder.

3.2 SYNTHESIS METHODS

a) Powder preparation

b) Ball milling

c) Powder calcinations

d) Pelletization

e) Sintering of pellets

f) Density and porosity measurement.

3.3 CHARACTERIZATION TECHNIQUES

a)X – RAY diffraction study,

b) Raman spectroscopy

c) Scanning Electron Microscopy study

d) Dielectric study

3.4Raw materials used for synthesis

Table-1: Details of chemicals and raw materials

Chemical Name	Chemical Formula	Purity	Source
Bismuth oxide	$Bi_2 O_3$	99.9%	S.P. Fine Chemical Ltd., Mumbai
Sodium carbonate	Na_2CO_3	≥99.5%	Loba Chemicals Pvt. Ltd., Mumbai
Titanium oxide	TiO_2	99.9%	Merck Specialties Pvt. Ltd., Mumbai
Calcium carbonate	$CaCO_3$	99.98%	S.P. Fine Chemical Ltd., Mumbai

3.5Preparation of powder by solid state synthesis route

Solid state synthesis method is adopted due to its easiness of processing than any other synthesis route.The raw materials are weighed in stoichiometric ratio to begin with synthesis process.

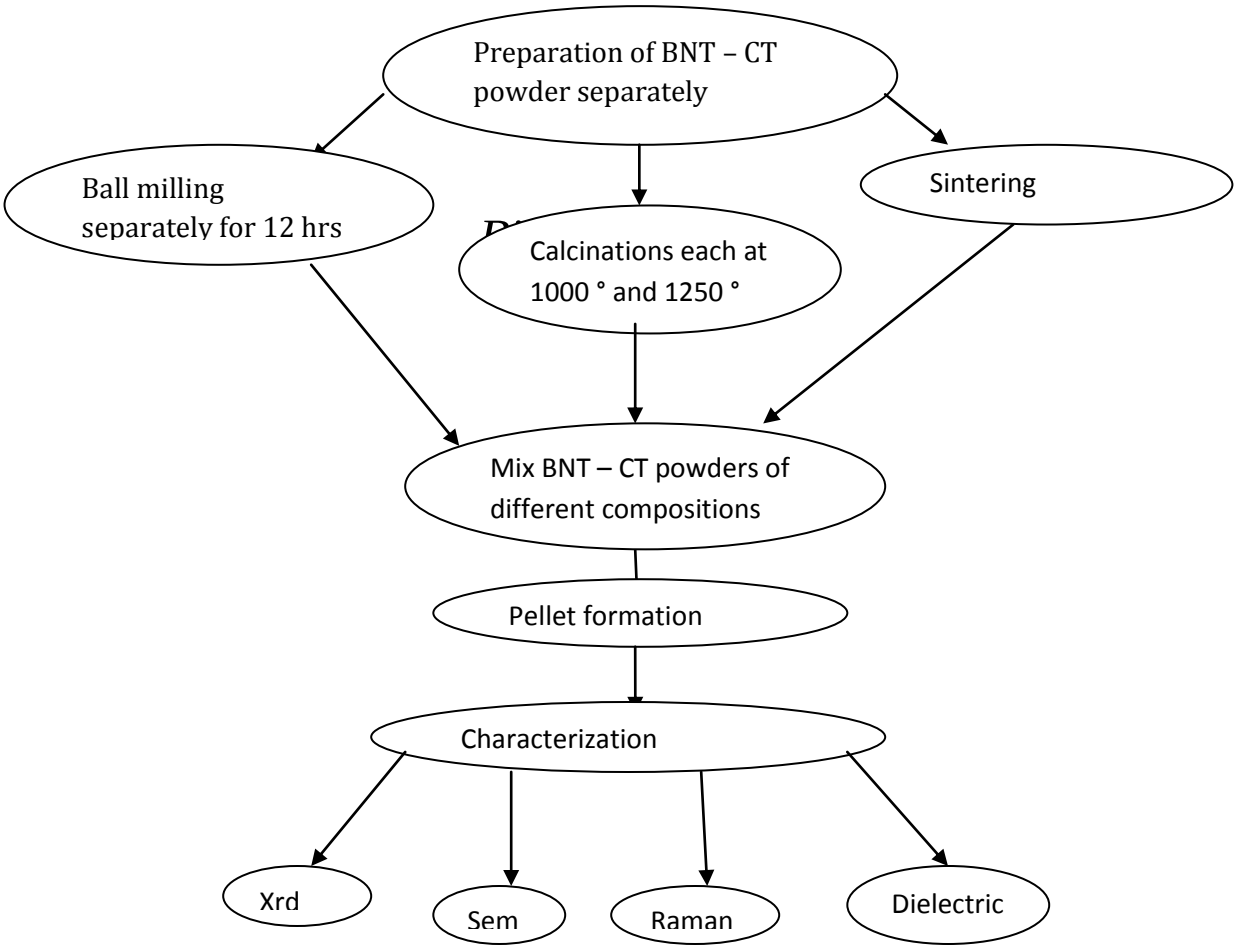
The balanced chemical equation of Sodium bismuth titanate is

$$Na_2CO_3 + Bi_2O_3 + 4\,TiO_2 \rightarrow 4\,Bi_{0.5}Na_{0.5}TiO_3 + CO_2\uparrow$$

The balanced chemical equation of Calciumtitanate is

$$CaCO_3 + TiO_2 \rightarrow CaTiO_3 + CO_2\uparrow$$

3.6 Flowchart of powder preparation



3.7 Explanation of different synthesis methods

Ball milling

The BNT and CT powders were ball milled separately for twelve hours using zirconia balls and acetone as a medium and thenwere left for drying and then the balls and powders were separated out. By ball milling the materials are grinded into fine powder. During the process of ball milling high energies are released due to the difference in speeds between the zirconia balls and the grinding jar.

Calcination

The BNT and CT powders were taken in separate alumina crucible .The BNT powder wascalcined for 2 hours at 1000^{o}C and the CT was calcined for 2 hours at 1300^{o}C. The main purpose of this calcination is to drive out water, carbon dioxide from the powder sample.Thermaldecomposition takingplace at a temperature below the temperature of melting pointis called calcination where phase change occurs and the volatile substances are removed out. The furnaces used for calcinations are shaft furnaces, rotary kiln etc.

Mixing different compositions of BNT with CT

BNT-CT compositions were made by using the formula (1-x) BNT-x CT with different weight fractions of CT taking x=0.01, 0.03, 0.05, 0.07, 0.09.

Pellet formation

Thecalcined powders of different composition were mixed by using distilled water. The powder was then mixed with PVA binder and grinded for four hours continuously. After drying it was

scraped out from the agate mortar and were separately packed. Then pellets were made by the help of a dieset and a pelletize under a load of 5 ton.

Sintering

The prepared pellets were sintered at 1100^{o}C in a furnace.Sintering is done to densify the pellets and improve its strength. The sintering also causes the diffusion of atoms which will help in grain growth and re crystallization. The decrease in porosity is also observed. The type of furnace used is an electrically heated one. Walking beam furnaces are preferred for higher temperatures. To get good result it is necessary to control the heating rate and temperature.

Density and porosity measurement

The density and porosity measurements for different compositions of BNT – CT were calculated by using the formula

$$\text{Density} = \text{dry}/ (\text{soaked} – \text{suspended})$$

$$\text{Porosity} = (\text{soaked} – \text{dry}) / (\text{soaked} – \text{suspended})$$

3.7 Explanation of different characterization techniques

X- Ray diffraction study

X-rays are electromagneticradiations having wavelength smaller than that of visible light. X-ray diffractometer works on the principle of Bragg's law which is given by

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

Where, d is the spacing between atomic planes, λ is the wavelength of x-ray used and ɵ is the angle of diffraction.

n =1, 2, 3

The x-ray diffraction is a technique used to determine different phases present in the sample, crystal structure and the crystallite site.

The pellets having different compositions of sodium bismuth titanate and calcium titanate were subjected to x-ray diffraction and the results were obtained.

Scanning Electron microscopy study

In SEM 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 converted into signal that displays on a screen. As the samples are non-conducting, a thin layer of platinum is coated using a sputter coater. Generally SEM only provides information about the surface of the specimen and not the internal contents. SEM can't scan deep into the surface. In this case the sample size is thick. It focuses on small area of the sample. This characterization technique provides information regarding surface morphology of the sintered pellets.

Dielectric Study

For dielectric measurement Salatron grain/ phase impedance analyzer was used. The data was taken by interfacing the Salatron grain / phase impedance analyzer and the data was collected as a function of frequencies at different temperature.

Raman Spectroscopy Study

Raman spectroscopy is a technique by which we can study the vibrational and rotational modes in a system. The spectral lines have frequencies greater than or lesser than the original frequencies. Frequency in raman lines are not determined by the scatterer but by the incident frequency. The most important point of Raman spectroscopy is that the Raman lines are strongly polarized.

CHAPTER-4

4.1 X- Ray diffraction analysis

Fig.4.1 shows the XRD patterns of the (1-x) $(Bi_{0.5}Na_{0.5})TiO_3$-$xCaTiO_3$ceramics with $0 \leq x \leq 0.09$. As can be seen, all the samples show pure perovskite structure, suggesting that $CaTiO_3$ diffuse into the $(Bi_{0.5}Na_{0.5})TiO_3$lattice to form a solid solution. All the patterns are indexed with the standard pattern of JCPDS card no.36–0340. With increasing the concentration of CT the peak is shifting towards the higher angle indicating that the lattice parameter is decreasing. Due to the decrease in the lattice parameter the structure remains same.

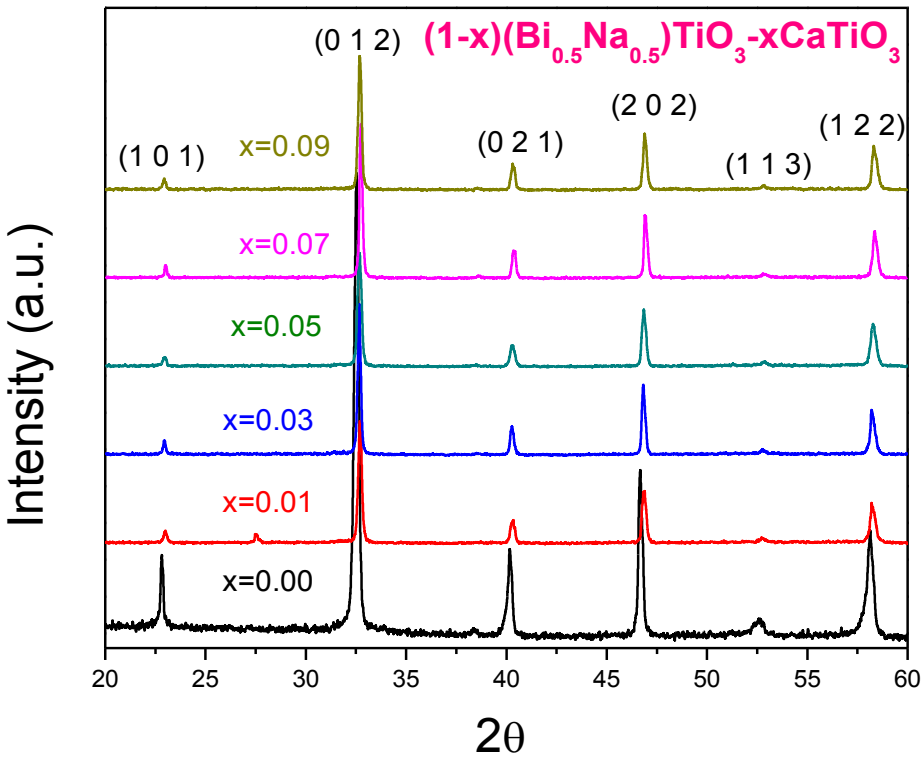


Fig.4.1 XRD pattern of (1-x)BNT-xCT ceramics

4.2 Scanning Electron Microscopy analysis

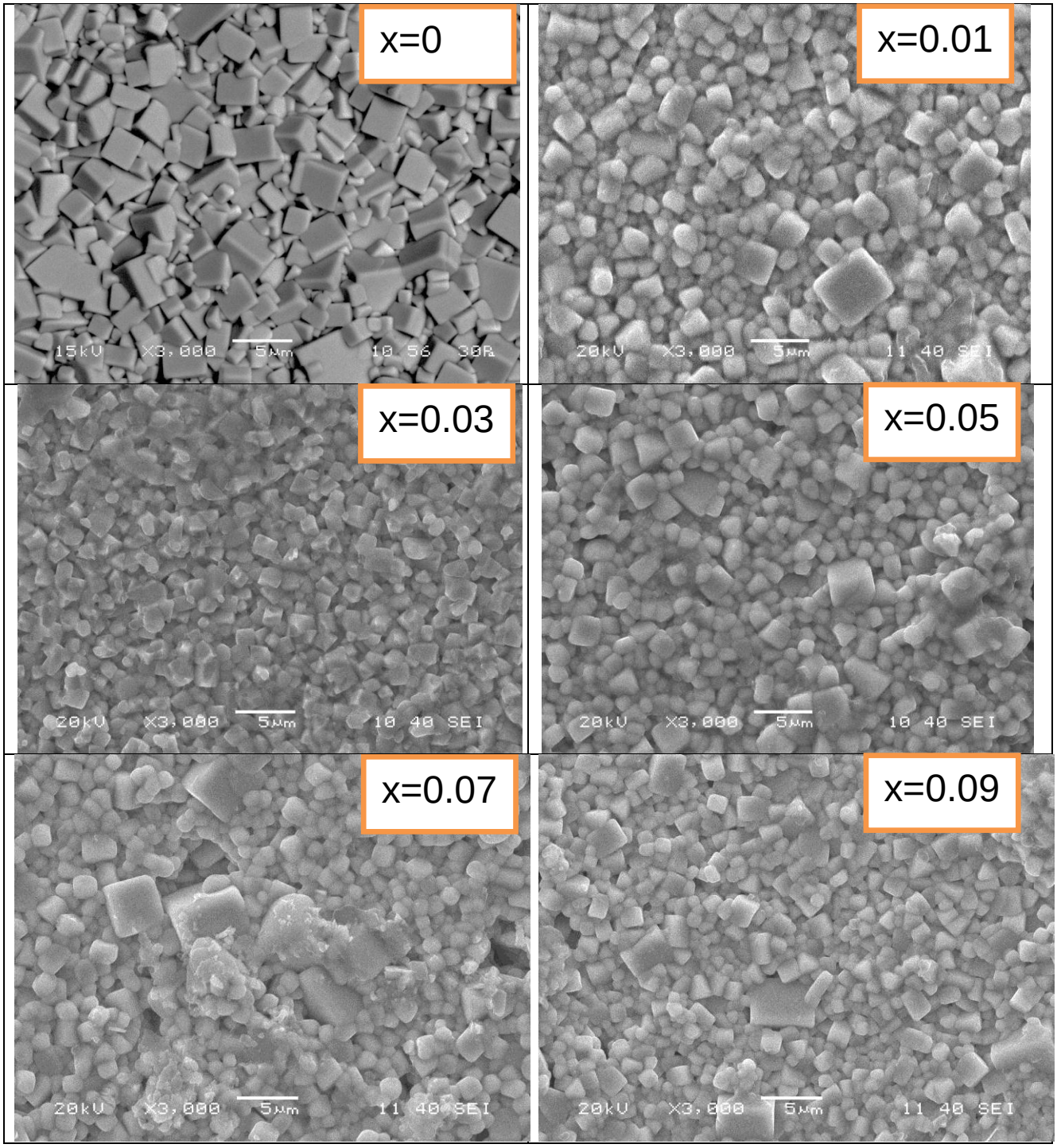


Fig.4.2 SEM micrograph of (1-x) BNT-xCT, for x = 0, 0.01, 0.03, 0.05, 0.07 &0.09

SEM micrographs for the pure BNT and (1-x)BNT-xCT ceramics with $0 \leq x \leq 0.09$ sintered at 1100º C for 2 h are shown in fig. 4. It can be seen in the Fig. 3(a), rectangular grains are present in the surface of the pure BNT ceramics. An addition of small amount of CT contributed to smaller grain size and rectangular grains almost changed to semi spherical with average grain size of 2-3 micrometer.With further increase in the CT concentration the average grain size remains relatively same and with CT concentration of 0.09, the average grain size is decreasing to 2 micrometer as is seen in Fig. 3(b-f). This result indicated that solid-solution with a small quantity of CT is effective in suppressing the rectangular grains and grain growth of BNT ceramics.

4.3Raman Spectroscopy analysis

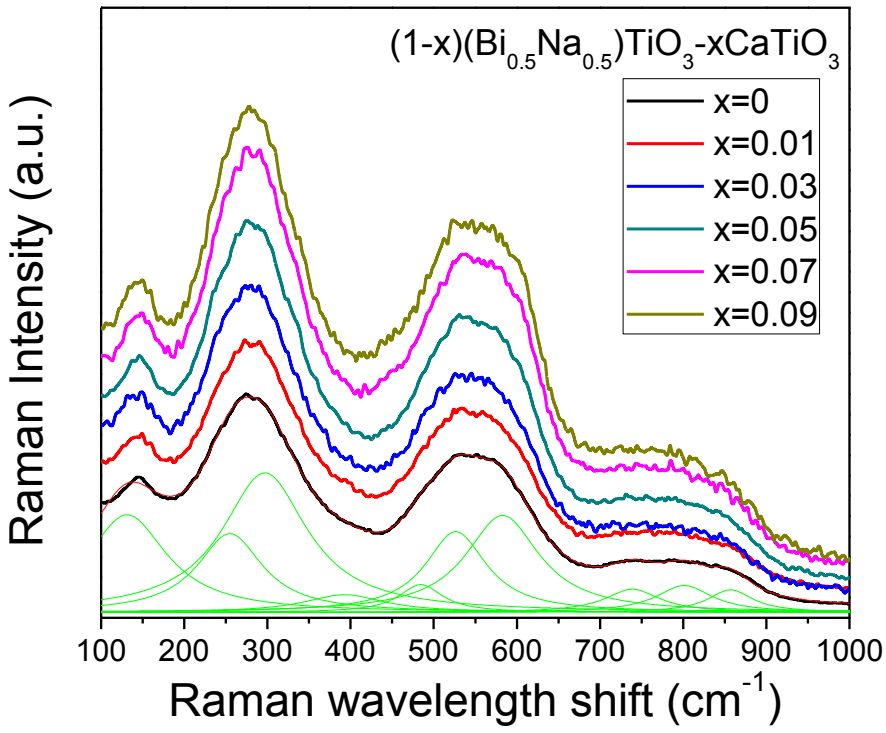


Fig. 4.3 Raman Spectroscopy study of (1-x) BNT-xCT ceramics

As per the Group theory analysis, BNT (rhombohedral, R3c) should show 13 Raman active modes; in irreducible representation $\Gamma_{Raman} = 7A_1+6E$.Therefore, among the 13 Raman-active vibrational modes it is possible to observed 10 Raman-active modes from fitting of the Raman spectrum of BNT and all the compositions of BNT-CT ceramics with to the (only Lorentzian Area function). This can be attributed to the A-site disorder and the overlapping of Raman modes due to the lattice anharmonicity. The Raman patterns shows roughness or irregular due to the data taken in high resolution, it makes noise during the collections of data. If we take the data in low resolution impossible to distinguished the closely bounded molecules.

4.4 Dielectric analysis

The fig. below shows the relative permittivity vs. temperature and dielectric loss vs temperature for (1-x) BNT–xCT with CT concentrations 0.01 and 0.03 respectively. Both in 0.01 and 0.03 composition of CT the relative permittivity increases with increase in temperature upto a certain level which corresponds to a transition from rhombohedral to tetragonal. On further increasing the temperature the dielectric constant decreases resulting in a transition from tetragonal to cubic. The graph of dielectric loss vs. temperature is sufficient to transfer the ions to the vacant sites of oxygen, due to which the conductivity increases and there is dielectric loss with increase in temperature.

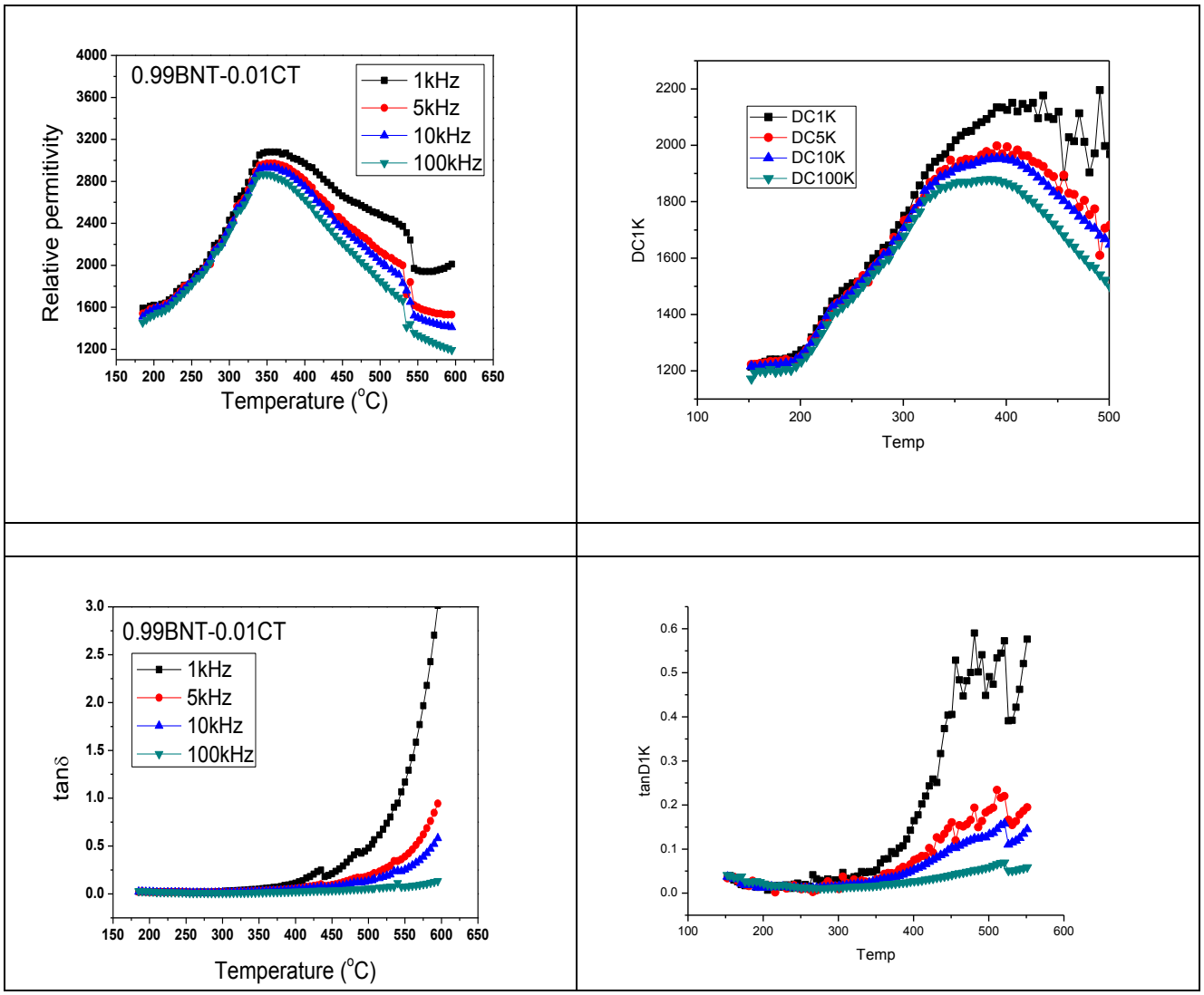


Fig.4.4 Dielectric study of (1-x)BNT – xCT

CHAPTER – 5

Conclusion

- Single phase Perovskite BNT, CT and (1-x)BNT-xCT ceramic successfully prepared through solid state reaction route.
- XRD patterns revealed that the peaks shift towards higher angle with increase in the concentration of CT.
- Raman study shows that with increasing CT concentration distortion and flattened in the peak occurs indicating the decrease in lattice parameters.
- SEM micrographs show that with increasing the concentration of CT the average grain size decreases and shape changes from rectangular to quasi-spherical.
- Dielectric study shows that with increase in CT concentration, the transition temperature, dielectric loss increases and dielectric constant decreases for a particular frequency.

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