Structural, Optoelectronic and Ferroelectric behavior of A & B site modified BaTiO₃

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By

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A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> *by* **Prashant Gupta**



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Structural**, **Optoelectronic and Ferroelectric behavior of A & B site modified BaTiO**₃ in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF PHYSICS**, **Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July,2019 to June,2020 under the supervision of Dr. Somaditya Sen, Associate Professor.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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Abstract

Ferroelectric barium titanate (BT) possesses a high dielectric constant coupled with good thermal stability. Therefore, it is an interesting material for applications such as multilayer ceramic capacitors, piezoelectric and pyroelectric sensors or dynamic random-access memories (DRAM). It is the first discovered ferroelectric perovskite. It has the classic ABX₃ (with Ba²⁺ as A and Ti⁴⁺ as B) perovskite structure. There are many studies reported for properties of BT ceramics, some reports are focused to increase its Curie temperature and dielectric constant, and some are focused on increasing its ferroelectric properties. In the present work we have modified the BT ceramics with Ca, V, Cu and Bi, Cu doping.

Modified BaTiO₃ ceramic Samples Ba_(0.9)Ca_(0.1)Ti_(1-3x)Cu_(x)V_(2x)O₃ (BCTCV) and Ba_{1-x}Bi_xTi_{1-x}Cu_xO₃ (BBC) have been synthesized via Solgel method. The X-ray Diffraction (XRD) of samples were done to confirm its formation. Vibrational modes of the samples are studied and verified by the Raman spectroscopy. The dielectric constant (ε) and dielectric loss ($tan\delta$) have been measured for both samples. The variation of dielectric constant and dielectric loss as a function of temperature has been studied. Optical properties of the samples are studied using the diffused reflectance spectroscopy. The ferroelectric nature of the ceramics have been confirmed by P-E hysteresis loop study. FESEM on the samples were done to check the surface morphology of the sample. To have a modified BT ceramic with relatively higher Curie temperature and comparable dielectric constant, can be great aid in many technological advancements. Better PE loop response is also desired for many applications such as storage devices. Rising T_c was confirmed by temperature dependence of the dielectric constants study. This is one of very few examples for rising T_c in the solid solution based on BaTiO3 except for doping of Pb^{2+} ion.

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ACRONYMS

BT:	BaTiO ₃
BBC:	$Ba_{(1-x)}Bi_{x}Ti_{(1-x)}Cu_{x}O_{3}$
BCTCV:	$Ba_{(0.9)}Ca_{(0.1)}Ti_{(1-3x)}Cu_{(x)}V_{(2x)}O_3$
MLC:	Multi Layer Capacitors
FESEM:	Field Emission Secondary Electron Microscopy
NIR:	Near Infra-Red
UV:	Ultra-Violet
DRS:	Diffused Reflectance Spectroscopy

Chapter 1

INTRODUCTION

1.1 Ceramics-an introduction

A ceramic is an inorganic compound of metal and nonmetallic with covalent or ionic bonding, that have been formed and afterward solidified by heating to high temperature. When all is said and done, they are hard, corrosion resistance, and fragile materials. "Ceramics" is gotten from the Greek word "keramikos" meaning pottery. It is identified with the more established Indo-European language signifying "to burn". Therefore, it was utilized to allude to an item that got through the activity of fire upon earthen materials. Ceramics can be characterized as inorganic, non-metallic materials that are regularly delivered utilizing mud and different minerals from earth or synthetically handled powders. Ceramic can be crystalline and are compounds of metallic and nonmetallic elements[1]. Glass is sometimes considered as a subset of ceramic due to its amorphous state and short crystalline order[2]. Ceramics can be formed either by the action of heat or chemically synthesizes at low temperatures using for example, hydrothermal or sol-gel synthesis. Ceramics are further classified by their useful properties.

• Electro-ceramics: The term electro ceramic refers to all those ceramics which are useful due to their electrical properties. These properties arise due to the composition and microstructure of these materials. Their properties can be tuned with the incorporation of temperature, stress, the chemistry of surrounding material. They govern all most 90% of the advanced ceramics today as their qualities can be tuned to make passive devices, sensors, and actuators[3].



• **Structural ceramics:** Ceramics that are used for components that have severe "structural" design constrain. These materials have high-temperature strength, high-temperature stability; wear resistance, chemical inertness, and corrosion resistance. These are made from synthetic powder that can be tuned as per specific requirements. Due to its vast popularity, they govern approximately 10% of all the advanced ceramics today[4].



Figure1.2:applicationsofstructuralceramics[ref:https://www.inceramics.com.pl/index_en.html]

Bio-ceramics: These are the ceramics that are biocompatible, inert to the human body, and are an important subset of biomaterials. They are been used in Rigid material in Surgical implants, though some bio-ceramics are flexible also. Bio-ceramics are closely related to either the body's materials or are extremely durable metal oxides[5].



Figure 1.3: typical bio-ceramics used in the human body [ref: K. ISHIKAWA and S. MATSUYA et al.(2003)Volume 9; (ISBN: 0-08-044150-5); pp. 169]

• Thermal barrier coating: As ceramics have very poor conductivity/ high resistance they are used as ceramic coating usually on a metallic surface, operating on high temperature to limit the thermal exposure of structural component, extending part life by reducing oxidation and thermal fatigue[3].



Figure 1.4: Schmitt diagram of the thermal barrier coating

In the Following thesis, we have focused on electro ceramics as it's the majority of the whole. Electro ceramics dominate the market because they have various advantages as they can be used in multiple applications and the most common thing in all the applications are their dielectric properties and we'll discuss that in detail.

1.2 Dielectrics

The ceramic materials that have very high electric resistance or very low conductivity are called Dielectric materials. Effectively they don't possess any free electron. The mono-atomic material is made of an atom, they have positively charged nucleus an around it negatively charged electrons in most of the element, the number of electron and proton are equal, the center of both the charges coincides and hence they have no net charge known as polar molecules. On the other hand, polyatomic material is made of molecules, in molecules, the center of all the positive charge distribution may or may not coincides with the center of negative charge distribution also known as non-polar molecules. When two opposite charge are some distance apart, they produce dipole moments \vec{p} . The dipole moment per unit volume is called Polarization \vec{P} . Whereas every other Molecule can possess dipole in a different direction due to random thermal agitation, as in a sample we can have thousands and millions of those random dipoles, so net dipole moment is affectively always zero. Now when this material is placed in a uniform electric field, É both charges felt a force but in a different direction due to their charges as force, $\vec{F} = q\vec{E}$.

Now they will try to align in the direction of electric filed due to torque by this force and thermal agitation will still try to randomize the orientation and due to this, we get partial alignment, as a result, we get a non-zero net dipole moment in the dielectric material. This polarization is proportional to the electric field applied, when we remove the sign of proportionality, we get a constant.

$$\vec{P} \propto \vec{E}$$
$$\vec{P} = \varepsilon_o \chi_e \vec{E}$$

Here ε_0 is called the permittivity of free space and χ_e is called electronic susceptibility. Now the polarization can be produced in the system by different means it depends on the system and its microstructure that what

kind of polarization will be produced in it. Here are the few main types of polarization.

1.2a Electronic Polarization

When we have a mono-atomic metrical which has an evenly spread electron cloud around them, they have a zero net dipole moment, now as we introduce the electric filed the polarization is the material increases proportionally[6]. When we remove the proportionality, we get a constant α , known as the polarizability of the material.

$$\vec{P} \propto \vec{E}$$

 $\vec{P} = N\alpha_e \vec{E}$

Here α_e is the electronic polarizability and \vec{E} is the applied electric field. Here α_e can be written as:

$$\alpha_{\rm e} = \frac{{\rm e}^2}{{\rm m}(\omega_0^2 - \omega^2)}$$

Here α_e is the electronic polarizability e is the charge of an electron, m mass of an electron, ω_0 is the natural frequency of the material and ω is the frequency of the applied signal. As we can see electronic polarizability does not depend on temperature. It provides with the most contribution to the dielectric constant at high frequency.



Figure 1.5: Electronic Polarization.

1.2b Orientation Polarization

It is produced in a material which already has some permanent dipole moment but due to thermal agitation net dipole moment is still zero, as soon as these materials are placed inside an electric field, they start to align themselves to the field due to produced torque and produced net dipole moment. It is also called dipolar polarizability[7]. It only contributes at a lower frequency as at higher frequency the dipole cannot align with the applied field in time and it freezes out. It is more important in gas and liquid phase compare to solid as they are so closely packed in solid that it is very unlikely to have a permanent dipole moment. Polarizability α_d is given as[8]:

$$\alpha_{\rm d} = \frac{\vec{p}^2}{3k_{\rm B}T}$$

Here α_d is dipolar/orientational polarizability, \vec{p} is dipole moment, T is temperature and k_B is Boltzmann constant.



Figure 1.6: Orientational Polarization.

1.2c Atomic or ionic Polarization

Unlike polar material, Ionic material does not have any dipole moment due to their evenly shared charges. They have no net dipole moment whatsoever in the absence of electric field, when the field is applied both the charged ions go opposite sides, they create a local electric field \vec{E}_{LOC} , which creates net polarization in the system \vec{P} . If we have N_idipole in the material than total polarization can be given as:

$$\vec{P} = N_i \alpha_i \vec{E}_{LOC}$$

Ionic polarizability can also be given by the Clausius-Mossotti equation.

$$\alpha_{i} = \left(\frac{\epsilon_{r} - 1}{\epsilon_{r} + 2}\right) \frac{3\epsilon_{0}}{N_{i}}$$

Atomic or ionic polarizability (α_a) is given by the born equation.

$$\alpha_{a} = \frac{e^{2}2\pi}{\omega_{0}^{2}a^{3}} \left(\frac{1}{m} + \frac{1}{M}\right)$$

Here α_a is atomic polarizability, e is the charge of an electron, a isthe nearest neighbor distance, m and M is masses of two ions and ω_0 is the absorbed frequency. Ionic polarizability is more dominant than electronic polarizability which means ionic material may have more dielectric constants[9].



Figure 1.7: Ionic polarization.

1.2d Space Charge Polarization

Charges that are trapped within the material, at the grain boundary of the bulk material or the interface of different materials are called space charges. Space charge polarization effects free charges whereas electronic and ionic affect bound charges (i.e. ionic and covalent bond), It is more prominent in the bulk material dielectrics which have amorphous or poly-crystalline structures. space charge polarizability is given as $\alpha_{\rm C}$.

$$a_c = \alpha - \alpha_e - \alpha_d - \alpha_i$$

Here α is the total polarizability so the total can be written as:

$$\alpha = a_c + \alpha_e + \alpha_d + \alpha_i$$

So, the total polarization of material depends on α . According to the system and its environment (Temperature and frequency), there will be some polarizability that will be more dominant than others which essentially give rise to change in polarization and hence dielectric constant with varying temperature and frequency[10].



Figure 1.8: Space charge polarization.[ref:<u>https://www.researchgate.net/figure/7-The-interfacial-Space-</u> charge-polarization-in-dielectric-materials_fig6_264928627]

1.2e Dielectric Constant

Now we studied diffrent kinds of ways that can cause polarization temporarily or permanently. But in most of the cases, net polarization is Zero. It is when the material is placed in an electric filed the field cause force in two different direction due to different charges. Which later produces torque to align the dipole moment in the direction of the applied field. As all the charges start to separate it creates an extra layer of surface charges at the end of the material. Now due to displaced charge, there is another local electric field in the sample which will be opposite to that of applied. So, the total field in sample is now less than the applied electric field. The ratio of this electric field applied to the total electric field is called Dielectric constant or relative permeability of the material [11]. It is a unit less quantity that determines the charge storage capability of a material. When dielectric material is placed inside an capacitor of capacitance C. It increases the capacitance with multiple K. We can also see it in this way, it is the ratio of capacitance with dielectric and vacuum.



Figure 1.9: Dielectric constant[ref:https://www.doitpoms.ac.uk/tlplib/dielectrics/dielectric_constant. php]

As all the ceramic have high resistances but dielectric constant more depends on the microstructure and how molecules are bound with each other. No D.C. currents pass through it due to its high resistance. When you apply A.C. source across a dielectric material, the induced charges will get affected and change their direction accordingly which will cause a little A.C. signal to pass[12]. As you change the frequency of the signal the charges that displaced due to the electric field also have to change their direction accordingly and have to travel in between the sample going from one end to another. There are few things can affect the value of the dielectric constant of a material such as temperature and frequency. As you increase the temperature the thermal agitation in the material increases, as a result of that the dipole again starts to come to their original position and the net dipole moment starts to fall and so the dielectric constant. Now when the frequency is increased it takes some time for the dipole to change their direction due to which, at the high frequency they cannot cope up with the frequency of the signal, and net polarization decreases. The dipoles don't realign in time and dielectric constant decreases. Frequency effect differently on different polarizations ,as total polarization is the sum of all individual polarization and each has their dominant areas of frequency and temperature. As a result, the value of total polarization decreases with an increase in temperature and frequency both.



Figure 1.10: Frequency-dependent dielectric constant

1.2f Dielectric Loss

It is said that dielectric material has a very high resistance and no current passes through them we only have a displacement of charges so we have current leading the voltage with 90° phase, but due to charges at the grains, space charges, electronic polarization, ion deformation or ion migration a small current passes through. So now the current lead the voltage with 90°- δ , here δ is the additional phase difference also called loss angle. As we have discussed dielectric constant is a complex quantity which has a real part (ϵ') and imaginary parts (ϵ'') as well and the total sum is called relative permeability of dielectric constant (ε_r) as we know it. $\varepsilon_r = \varepsilon' + j\varepsilon''$ The ratio of imaginary part to the real part is called loss tangent and is given as;

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

The quantity " ϵ_r *tan δ " is called the loss factor. The main factor that stands out in dielectric loss is the ion migration, both temperature and applied frequency affect the ion migration greatly. As you increase the temperature ion migration increases and which later cause the increase in dielectric loss. The ion migration is only dominant in low frequency as you increase the frequency it decreases which means at higher frequency there is low loss. The quantity tan δ differentiate between good and bad dielectric material because a material with low dielectric constant and low loss is always preferable than material with high dielectric constant is huge.

Now since we have study about dielectrics, there are different types of dielectric materials depending to their structure. We'll discuss them in detail.

1.3 Piezoelectricity

Piezoelectricity word originated from Geek word piezo which means to squeeze or to press. the material when it is pressed under external mechanical stress produces charges this phenomenon is called piezoelectricity. when charges are created by applying mechanical force it is called direct piezoelectricity, when applying an electric field to the material it changes the dimension of the material, it is called reverse piezoelectricity[14]. It originates from the micro scoping displacement of the charges from within the system. When an external force is applied to the material it deforms due to which charges get shifted and produces polarization and visa-versa. The direction of polarization depends on the direction of force. It was first introduces by Pierre brothers in tourmaline, topaz, quartz and Rochelle salt in. In solid-state we have a total of 32 types of crystal structure classes, out of 32, 21exibhites piezoelectric effect due to their non-symmetric structure. Now since due to the random orientation of the dipoles,The net piezoelectricity we'll be zero, to make ceramics net piezoelectric we do "poling" of material. In this, we first heat the material to temperature more than critical temperature than apply a very high electric field (few KV/mm) across the material. Above Curie temperature, every ceramic structure becomes symmetric, now due to the high electric field, the charges are forces to align in the poling (electric field direction) direction after that we cool it down below the curie temperature slowly and after some time remove electric field[15]. Now the charges is been shifted from its initial position and we have permanent polarization in the poling direction. Now the material will exhibit properties (responds to electric field and external force) like piezoelectric material like a single



crystal.



1.4 Pyroelectricity

Out of those 21 non-symmetric crystal structures classes, 10 system has a uniaxial polar axis, therefore, called polar crystal class. These materials have spontaneous polarization but can only be activated once uniform temperature change ΔT is applied. When you apply uniform temperature difference in these materials it changes their polarization[16]. When you change the temperature, it changes the structure a bit which changes spontaneous polarization if this change is constant then you'll get charge separation and hence electricity. Change is polarization $\Delta \vec{P}$ per unit change in uniform temperature is a constant γ called a pyroelectric constant.

$$\Delta \overrightarrow{Ps} = \gamma \cdot \Delta \overrightarrow{1}$$

It does not matter whether you are heating the sample or cooling it as far as the rate of change of temperature is constant you will get the same current in both the cases it's just direction of current will change[17]. In these materials, the direction of polarization cannot be changed by applying an electric field in different directions and polarization is only dependent on temperature only.



Figure 1.12: pyroelectrical properties.[17]

1.5 Ferroelectricity

These are non-symmetric materials with polar axis thus they have spontaneous polarization as it was in case of pyroelectric material but in ferroelectric material, you can change the direction of polarization by applying an electric field in a different direction and ferroelectric materialtend to retain the polarization even after removing the electric filed, hence you get PE hysteresis loop[18]. It was first observed in Rochel salt by Valasek. They have certain domains with a certain direction of polarization and as you apply electric field they all try to align to electric filed very quickly, due to domains of same polarization, ferroelectric material can switch to opposite polarization in fastest time in all of the dielectric materials, and they retain the direction of polarization even after removing the applied electric field which makes them suitable for many applications. Ferroelectric material under a specified temperature called curie temperature behaves as a ferroelectric material, after curie temperature every ferroelectric material behaves as a paraelectric material and losses its desirable quantities.

15.1 PE HYSTERESIS LOOP

When you first apply electric field in the starting, all the dipole that are scattered in random directions starts to align in the direction of applied electric field and after a certain value, they possess its maximum polarization P_{max} polarization will not increase no matter much more electric field you apply because there is no more domain to align, now when you start to decrease the electric field the polarization decreases but not with the same rate it was increased, at electric field E=0, there is still some polarization left in the system which is called remnant polarization Pr because dipole domain provides with more resistance towards the polarization change than an individual dipole. Now to get the polarization P=0, we further change the direction of electric field and apply it in opposite direction now the polarization decreases and becomes zero, this value of electric field is called coercive electric filed E_c. Now when we further decrease electric field and we again get maximum polarization in opposite direction -P_{max}. Now there is no more dipoles to align. we again decrease negative electric field and get -P_r than increase the positive filed to get E_c at which polarization is zero, again increasing the electric filed we get back to the maximum polarization, and hence we got our famous PE hysteresis loop.



Figure 1.13: PE Hysteresis loop[ref:<u>https://www.globalsino.com/EM/page3544.html]</u>

When a ferroelectric material is been placed between a parallel plate capacitor it increases its dielectric constant significantly as it can switch polarization with a change in the applied electric field very fast. The dielectric constant is given as:

$$\varepsilon_{\rm r} = \frac{\rm C}{\rm C_0}$$

$$C_0 = \frac{\epsilon_0 A}{d} \qquad \qquad \chi_e = \frac{c}{T_c - T} \qquad \qquad \epsilon_r = (1 - \chi_e)$$

Here χ_e is the electric susceptibility of the material, ε_0 is the permittivity of free space, ε_r is the relative permittivity also called dielectric constant, C is capacitance with a dielectric material, and C_o is with vacuum, A is the area of capacitor plate, d is the separation between plates, T is the temperature of the material T_c is the curie temperature of the material and c is the Curie constant. Ferroelectric material follow Curie-Weiss law which means that after a certain temperature T_c called as curie temperature the material is no more ferroelectric, we get maximum dielectric constant (ε_m) at that temperature, due to heat the material goes from a non-symmetric polar state to a highly symmetric non-polar state and losses its ferroelectricity.

ferroelectric materials have a certain kind structure to perform its qualities, they can be differentiated according to their symmetry such as; layer structure, perovskite structure, pyrochlore structure, tungsten bronze, etc. out of which perovskite structure is most dominant and we will discuss that in great details.

1.6 Perovskite oxides

The material that has ABX₃ type of structure, where A is large cation and B small metal ion and X is an anion that can be either oxygen or Florence, is known as perovskite structure. Atomic structure ABO₃ was first observed in CaTiO₃.A-ions are having 12coordination number with B-ions and B-ions is with octahedral configuration with Xions. Octahedral configuration is the main cause of many technologically advantages of these materials[19]. The most famous members of this structure are BaTiO₃, PbTiO₃, SrTiO₃, and PbZrTiO₃ due to their phenomenal qualities.



Figure 1.14: Perovskite Structure

In these materials, as B-ions is in the octahedral configuration, there is a shift of central B-ion in either up or down direction, in Helmholtz free energy Vs polarization graph, there is two minima's available of polarization which corresponds to two stable structures which are $\pm \delta$ on Z-axis[20].



Figure 1.15: Free energy density as a function of 1-D polarization.[20]

An important factor to characterize perovskite structure is called a tolerance factor (t), which essentially tells us how perfectly the constituent atoms are structured to give a perfect perovskite structure. It is the ratio of octahedral cage width and anion-cation bond length.

Perovskite structures are cubic ideally and tolerance factor for a cubic structure is 1 and it is the maximum value of tolerance factor. Tolerance factor (t) is given as:

$$t = \frac{r_B + r_A}{\sqrt{2}(r_x + r_B)}$$

Ionic radius, of A, B and X are r_A , r_B , and r_X respectively, the knowledge of tolerance factor is crucial, perovskites structures have t=1 for pure cubic material. Structure with less tolerance factor has lower symmetry. If t>1 the structure would be hexagonal, for 1<t<0.95 it is cubic

to tetragonal, for 0.95<t<0.7 structure would be orthorhombic or rhombohedral.

1.7 Technological importance and Application of Ferroelectric Materials

The ferroelectric material is been used in many industries because it is the ultimate solution for energy conservation, energy conversion, storage devices, and many more. Since every ferroelectric material is pyroelectric and piezoelectric and a good dielectric material it has all the qualities to be used as an all go material, and this is the reason why they dominate the market and research community altogether.





Ferroelectric materials have so many applications and we are going to list a few of them it is to always take in mind that they are just a few most famous wide varieties examples the application of ferroelectric materials are countless.

a). Dielectric material: Due to high dielectric constant and more than room temperature curie temperature, ferroelectric materials are used in the multi-layer capacitor (MLC) and super capacitor for energy storage applications.

b). Ferroelectric memory: Die to quality that only ferroelectric material can retain the polarization even after removing the electric filed gives them the advantage to be used as a memory storage devices, we have

them in the market for a long time, we can polarize certain area in material in different orientations which can be later read as bit.

c). Transducers: Devices that convert one form of energy to another form of energy are called transducers. Due to their ability to convert applies stress (mechanical energy) and temperature (thermal energy) to electric energy and vice-versa, so ferroelectric material can be used as transducers.

d). Actuators: the device which is responsible for controlling the movement of the system. Ferroelectric material due to their piezoelectric quality can change the dimension in response to the applied signal they can be used as actuators.

e). Sensors: Since these materials can sense the change in the temperature and stress and can send the response as an electric signal and vice-versa so these can be used in a wide variety of sensors.



Figure 1.17: Application of ferroelectric materials.[ref: DOI: 10.1039/c3tc00597f]

You'll see that lead base ferroelectric materials such as Lead Titanate (PbTiO₃), Lead-Zirconium Titanate (PbZrTiO₃) and more of leadbased ferroelectric ceramics are most famous since lead-based ferroelectric material has better responses to all qualities such as hysteresis loop, high dielectric, piezoelectric and pyroelectric constant and many more, still the world is now doing research specifically on a lead-free ferroelectric material. Why? We'll discuss it here.



Figure 1.18: next step?[ref: https://www.sciencedirect.com/science/article/pii/S2352847815300083]

1.8 Why Lead-Free Ferroelectric Materials?

As we know that Lead (Pb) is a radioactive element, it's toxic and can have a very bad effect on human health and the environment as well. A severe exposer to lead can cause brain damage, attack the central nervous system causing memory problems, nausea, cause anemia, hypertension, constipation, headache, and can cause damage to reproductive organs. A vast exposure can cause coma and even death in some cases. The entire electronic waste can either dumped in-ground or in the sea, either way by direct contact or by raining it can go to our natural water reservoir and can pollute them causing us to be infected indirectly even when not in direct contact with lead. Due to these things, there is a great effort in the world to get a lead-free ferroelectric material that can
surpass or match the properties of lead-based ceramics and this is what we have tried to do that in this study.

1.9 Phase Transition

In a general way phase transition is referred to as the drastic change in one quality of material to another quantity. This drastic change can be observed while plotting quality to an increase in quantity, there is always a sharp peak or crest at the point of phase transition. These qualities mostly referred to as their structural parameters, different states of matter (i.e. solid, liquid, gas). In our case, it's the point in temperature range after which materially changes its structure and qualities related to that structure. The temperature at which the structure of material changes is called a phase transition temperature.



Figure 1.19: Phase transition.

1.10 Sintering

Sintering means that we must density the material to a maximum possible, to use it in any application we cannot bear any air or any impurity in the sample which can alter our results. Ceramics usually deal with very high temperatures, got their name from "To burn". In sintering what we do we mold annealed material with the help of palletizer into small disks of ~10mm diameter and thickness of few (~5-6) millimeters by applying the pressure of few (~1-2) tons by hydraulic pressing machine and carefully place them in a furnace to a temperature

approximately 100-200°C lower than its melting temperature for a certain time. It solidifies the material and we get a hard-dense disc of material that we can use for measuring properties of material further.

1.11 BARIUM TITANATE

Barium Titanate is the first discovered ferroelectric perovskite. Barium Titanate has the classic ABO3 (with Ba⁺² as A, Ti⁺⁴ as B and O^{-2} as X) perovskite structure. This is a centrosymmetric cubic structure with A at the corners, B at the center, and the oxygen at the face centers. The discovery of Barium Titanate was a breakthrough because, even though it is well known that ferroelectrics had very high dielectric permittivity the phenomenon had been confined to complex organic or hydrogen-bonded water-soluble solids which had symmetry, chemistry and physical properties unsuited to capacitor needs. Barium Titanate, on the other hand, is a stable refractory compound with a melting temperature approximately, 1680°C.Amongst perovskite structures, BaTiO₃ is particularly important due to its non-poisonous and ecologically noncontaminant nature. However, it has lower Tc, tetragonal to cubic phase transition temperature, than PbTiO₃ and PZT, predominantly toxic perovskites. So different endeavors have been put through to get a stable non-poisonous material with a high estimation of dielectric consistency and stability of tetragonal ferroelectric phase up to a higher temperature by doping a few foreign elements. Barium Titanate (BaTiO₃: BT) is strong perovskite ceramic ferroelectrics known to the scientific community for a long time. There are lots of potentials to be yet explored in these materials and to be used in the industry because of its noble properties owing to its perovskite structure. Ferroelectric ceramics are used in multilayer capacitors[21], ultrasonic transducers^[22], thermistors [23], optoelectronics[24], dynamic random-access memory[25], piezoelectric sensors, and memory device applications[25]. The tetragonality of such ferroelectrics is a signature of distortive properties and is measured by the lattice parameter ratio, c/a. The c/a ratio decreases with increasing temperature and finally at a phase transition temperature (T_c , Curie temperature) the distorted tetragonal phase changes to a centrosymmetric cubic phase. The ferroelectric properties are absent in the cubic phase. Hence, a higher T_c refers to more stable ferroelectricity up to higher temperature in the ceramic. BT has a $T_c \sim 121$ °C which is well established and is much lower than lead Titanate. Due to this factor, its applicability in high-temperature devices is limited due to low limits.

1.11.1 HISTORY OF BARIUM TITANATE

BaTiO3 is the most widely used ferroelectric material, and even sixty years after its discovery, it is the most important multilayer ceramic dielectric. BaTiO₃ was discovered during World War II in 1941 and 1944 in the United States, Russia, and Japan. At least in the U.S.A., the research was accelerated because of the war. At that time, mica was used in most capacitors, but U-boats threatened the supplies of mica to the U.S.A. from South America. The initial reports were based on doping studies of TiO₂ with BaO, which produced ceramic materials with enhanced dielectric permittivities. The mixed oxides were made by Thurnaurer and Deaderick at the American Lava Co. as early as 1941, U.S. Patent No. 2,429,588[26]. The high permittivities were found by measurements made at the Erie Resistor Company, with dielectric constant exceeding 1000, ten times greater than any other ceramic known at that time, such as TiO₂ (ϵ_r =110).

1.11.2 STRUCTURAL PHASE TRANSITIONS IN BARIUM TITANATE

For Barium Titanate the tetragonal structure is achieved by what is called a "displacive transition". The 'B' ions and 'A' ions are displaced from their cubic positions in one direction and the oxygen ions in the other direction. However, as the temperature is lowered, it goes through successive phase transitions to three different ferroelectric phases, each involving small distortions from the cubic symmetry. The Curie point TC, of Barium Titanate, is 120°C. Above 120°C, the original cubic cell is stable up to 1460. At 120°C, it undergoes a paraelectric to ferroelectric transition to a tetragonal structure, it is orthorhombic between 5°C and - 90°C and, finally, it is rhombohedral below -90°C. Each of these distortions can be thought of as elongations of the cubic unit cell along an edge ([001] or tetragonal), along a face diagonal ([011] or orthorhombic), or a body diagonal ([111] or rhombohedral). These distortions result in a net displacement of the cations to the oxygen octahedra along with these directions. It is primarily these displacements that give rise to the spontaneous polarization in the ferroelectric phases. Figure 1.20 gives the phase transition sequence in Barium Titanate.



1.11.3 PROPERTIES OF BARIUM TITANATE

Pure Barium Titanate (BaTiO3) ferroelectric ceramic material is an insulator with a large energy gap of - 3.05eV at room temperature. Barium titanate has become the basic ceramic capacitor dielectric material in use today. The main mode of its use has been in combination with other materials. Additions and substitution of alternative cations can have the following effects:

1. Shifting of Curie point and other transition temperatures.

- 2. Restriction of domain wall motion.
- 3. Introduction of second phases or compositional heterogeneity.
- 4. Control of crystallite size.

5. Control of the oxygen content and the valency of the Ti ion.

The major advantage of using Barium Titanate in various applications is that it can be used at places where lead-free ferroelectrics are in demand.

Chapter-2

Literature Survey

After getting the background of ferroelectric materials and their properties, we have done a literature review of pure and doped BT materials. In this chapter, we are going to discuss various results researchers got from doping different materials in pure BT. We have classified our review in the following parts.

- Barium Calcium Titanate based ceramics
- Barium Bismuth Titanate based ceramics
- Barium copper Titanate based ceramics
- Barium Vanadium Titanate based ceramics

2.1 Barium Calcium Titanate based Ceramics

 $CaTiO_3$ is been considered as one of the main perovskite structures, it is in the ferroelectric phase till ~150°C, therefore, various efforts have been done to get a sample that have good dielectric properties at relatively higher curie temperature.

M.B. gill et.al(2019) have synthesized Ca-doped Barium Titanate $Ba_{0.9}Ca_{0.1}TiO_3$ using a solid-state reaction method, where he explores the possibility of mechanical activation of the precursors. The sample was found to be in the Tetragonal phase with a reduction in crystallite size .he concluded that mechanical treatment can calcinate the sample at lower temperatures and with less amount to time[27].

Aanchalet.al.(2018) synthesized Ca-doped BaTiO₃ with 5,10 and 15 % doping using solid-state reaction method. He observed a decrease in the tetragonality of the sample with the increasing doping concentration because smaller crystal radius Ca^{+2} ions replacing larger crystal radius

Ba⁺².He also found that the average grain size of the sample was increasing with Ca concentration and there was a decrease in ferroelectric behavior with increasing doping concentration due to the decrease in Tetragonality [28].

Yukio et.al(2002). synthesizedBaTiO₃ with Cao (Ba_{1-x}Ca_x)_mTiO₃ ceramics (x: 0–0.10, m: 1.003–1.009)with 0.2 μ m diameter samples using hydrolysis method. They have reported an increase in the dielectric constant with doping. Internal stress from the grain boundary has suppressed the tetragonality of the sample as a result they are having high dielectric constant valu e [29].

M.R. Panigrahi and S Panigrahi (2009) have investigated the morphology of the Ca-doped BT, with $Ba_{1-x}Ca_xTiO_3$ (for x=0.05 to0.5) samples using SEM analysis. The increase of the doping concentration increase in the average grain size, having maximum grain size at 10% doping [30].

Seak-Hyun YoonEt.al.(2010) have synthesized a very strange composition using a solid-state reaction method. where they have investigated very fine-grained $(Ba_{1-x}Ca_x)TiO_3$ with only Ba site incorporation and $Ba(Ti_{1-x}Ca_x)O_3$ with only Ti site incorporation. They reported a decrease in lattice parameter a and c, so therefore no significant change in the c\a ratio and continuous increase in the Curie temperature for Ba site doped sample. Whereas for the Ti site doped sample, there is a slight increase in lattice parameter a and decrease in c which causes a decrease in the tetragonality (c/a). Curie temperature decreases continuously[31].

S.K. Pradhan et.al.(2015) doped Ca in a Barium Zirconium Titanate system (BaZr_{0.52}Ti_{0.48}O₃). They prepared Ba_{1-x}Ca_xZr_{0.52}Ti_{0.48}TiO₃ the sample using the sol-gel method. The dielectric constant was increased, and the dielectric loss was decreased with an increase of

Ca⁺²concentration.Diffuse phase transition is observed. The AC conductivity of the sample is also increased[32].

Sofia Sahooet.al.(2019) synthesized Ba_{0.92}Ca_{0.08}TiO₃using a solidstate reaction method and carried out temperature-dependent ferroelectric and dielectric measurements. The tetragonal to cubic transition is atalmost the same temperature but the other two transitions were shifted There is an increase in the remnant polarization and dielectric constant for 8% doped BaTiO₃[33].

2.2 Barium Bismuth Titanate based Ceramics

The doping in the Perovskite structure mainly depends on the crystal radius of the dopants. Dopant with higher crystal radius generally incorporates to the Ba^{+2} site where the lower crystal radius incorporates to the Ti^{+4} site.

L. Islam et al.(2015) have synthesized Ba_{1-x}Bi_{2x/3}TiO₃ with Bi₂O₃ as dopant using a solid-state reaction method. doping is used to lower the sintering temperature. The average grain size of the material is increasing with the doping concentration. The dielectric constant of the material is increased with the doping concentration continuously, but the dielectric loss is increased. Curie temperature is also increased and was max for 0.05% Bi doping[34].

N. Sareecha et al.(2017) have synthesized $Ba_{1-x}Bi_{2x/3}TiO_3$ with doping of Bi up to 1 mole% using a solid-state reaction method. The value of dielectric constant and transition temperature is increased.SEM analysis reveals that the samples are porous[35].

A. Mahapatra et al. (2014) have synthesized Bi-doped BaTiO₃ with the chemical formula $Ba_{1-x}Bi_{2x/3}TiO_3$ (x = 0.0, 0.01, 0.025, 0.05) using solid-state reaction method. All the samples were found to be in a single Tetragonal phase. Tetragonality (c/a) is increased as a result of that Curie temperature of the materials increased with the doping concentration. Whereas the value of the dielectric constant is decreasing. Diffuseness in the system is increasing with the doping concentration. The value of remnant polarization and coercive field is increasing with doping. The bandgap is decreasing and Urbach's energy tail is increasing due to extra oxygen vacancy and disorder due to Bi⁺³[36].

X.P. Jiang et al. (2007) have synthesized $Ba_{1-x}Bi_xTiO_3$ using a solid-state reaction method and studied temperature-dependent dielectric behavior and ferroelectric properties. At 15% doping, the material shows a relaxor type ferroelectric phase transition. The PE hysteresis loop also confirms that the sample shows relaxor type behavior at 15% doping concentration[37].

Shuangyi Liu et al.(2012) proposed a different approach for bismuth-doped barium titanate nanocrystal. $(Ba(Ti_xBi_{1-x})O_3)$ the crystalline nanocrystal is synthesized using a low-temperature solvothermal route which will allow substitution of Bi on the Ti site.XRD ,Raman Spectroscopy, SEM, and HRTEM characterizations are performed on the sample. Comprehensive analysis shows improved permittivity and lower loss[38].

Sadeghzadeh Attar A.et al (2016) synthesized $Ba_{0.5}Sr_{0.5}TiO_3$ using the sol-gel method and then study the effect of Bi-doping on this system. The average particle size of 35-40nm was obtained which is decreasing with the Bi- doping concentration. The temperature value at the maximum dielectric constant is shifting towards the lowers side and the value of the maximum dielectric constant is also decreasing with the increasing doping concentration[39].

2.3 Barium Copper Titanate based Ceramics

A. Mishra and NiyatiMishra(2012) have synthesized copper doped BaTiO₃ with chemical formula BaTi_{1-x}Cu_xTiO₃using a solid-state reaction method. Synthesized material was in the tetragonal phase, O-6 octahedra deformation mode is observed using FTIR which indicates

ferroelectric behavior. The transition temperature is been shifted to a higher temperature[40].

M.V.S. Rao et al. (2013) has also synthesized bi doped BaTiO₃ but he doped Cuon the Ba site of the material. Lattice parameters are decreasing, and c is increasing as a result, tetragonality(c/a) is increasing which increases dielectric constant. The increase of CuO in the system increases the dielectric constant of the system and dielectric loss is decreased. DC electrical resistivity decreased initially up to Tc and then increased. The sample indicates $Cu^{+2}-Cu^+$ ion in the conduction process around curies temperature [41].

Chen Ang et al.(1999) synthesized $BaTi_{1-x}Cu_xO_3$ using a solidstate reaction method. XRD patterns reveal that structure is changing with doping in becomes tetragonal to cubic as doping increases from 30% to 40%. At 50%doping concentration metallic conducting behavior was observed[42].

Ying-ChiehLee and Yen-Lin Huang(2009) doped Copper in $Ba_{0.6}Sr_{0.4}TiO_3$ system which already exhibits high dielectric constant and low loss tangent. Incorporation of CuO in the system reduces the sintering temperature very effectively and increases the density of the sintered samples. All the samples were in the tetragonal phase. Cu replaces the Ti site in the structure. For 0.6mole % the value lattice parameter is minimum, dielectric constant is a maximum and dielectric loss in minimum. The grain size of the material increases with the doping percentage[43].

2.4 Barium Vanadium Titanate based ceramics

Wei Cai et al.(2011) have synthesized Vanadium doped BaTiO3 sample by solid-state reaction method. V^{+5} ions replaced Ti⁺⁴ Ions On the Ti site. Doping accelerates grain growth, increases the curie temperature, decreases the dielectric loss. Remnant polarization of Vdoped BT ceramics increases reaches the maximum and then again decreases with the increase of doping concentrations. The value of coercive file decreases a little for doped samples with doping concentrations. Temperature-dependent Remnant polarization and coercive field both decrease with a rise in temperature[44].

P. Dulian et al. (2014) synthesized $BaTi_{1-x}V_xO_3$ using mechanochemical treatment using high-energy planetary ball-milling. Vdoping improves the functional properties as a capacitor. Increase permittivity and in a wide temperature range. It is having a diffuse phase transition[45].

F. Moura et al. (2008) have substituted V in the $Ba(Zr_{0.10}Ti_{0.90})O_3$ system using a solid-state reaction method. All the samples are in tetragonal phase structure. Remnant polarization increases and then decreases. Raman spectroscopy reveals that modes tend to disappear with doping concentration. The dielectric constant is maximum for 2mole % and decreases continuously after that [46].

2.4 Motivation for work

It is evident till now that 10% doping concentration of Ca in the BaTiO₃ system increases its qualities and have very little drawbacks till that doping %. Vanadium and Cu doping are also seen to increase, dielectric ferroelectric quantities, and apart from that it also helps in lowering the sintering temperature of the system. So, we have decided to synthesize Ba_{0.9}Ca_{0.1}Ti_(1-3x)Cu_xV_{2x}O₃ material and study their structural, vibrational, optical, dielectric, and ferroelectric properties to understand the system.

The various effort is been made to increase the ferroelectric to paraelectric transition temperature (T_c) of BaTiO_{3.} Individual dopants like Sr, Bi, Cu, Zr, Fe, lower T_{c.} Only by the doping of Pb the Tc is observed to increase but Pb is not environment friendly. However, it is reported that co-doping of a small concentration of Bi and Cu increases the Tc[10]. But

there is no extensive study about vibrational or electrical properties of the material. So, we have decided to synthesize Ba_{1-x}Bi_xTi_{1-x}Cu_xO₃material and study its structural, vibrational, optical, dielectric, and Ferro electrical properties.

Chapter-3

Synthesis Techniques and Sample Preparation

Required samples can be synthesized by using several synthesis techniques such as Solid-state reaction technique, hydrothermal and solgel, etc. During this project, we have used the Sol-Gel method to prepare all the samples due to its simple approach for making sample and we do not require any special expensive instrument to make a sample by it. It allows us to use low temperatures during synthesis thus, it is energy effective in that way. It results in a very high pure and proper stoichiometric sample with better control over the doping percentage. Sample preparation and calculation required to synthesis targeted material is been discussed in the following chapter.

3.1 Sol-Gel Synthesis Process

The sol-gel method is been used to prepare glassy and ceramic material at a very low temperature. It's been in the interest of researchers since the mid-1970s. The first synthesized glass from the gel was SiO2 base. In this process, we prepare a sol that is further heated to remove all the liquid in the fine inter-connected channels to get the gel. To make sol we make precursors of the needed elements by dissolving them in the appropriate solvent so that all the molecules are now strung in the solution in their Ion state and we get a colloidal solution. Now each of these precursors was mixed and stir for homogeneity and we have made our "Sol". Here we add two more compounds named as a gelling agent and a burning agent in the ratio of1:1. The solution of both creates monomer which upon heating will create polymers. Gelling agents provide a continuous chain of polymer on which Ion and metal are joined together. we have maintained the transparency of the solution by maintaining the acidity of the solution for homogeneity of the solution. We heat the solution with continuous stirring after dehydration, we are left with a semi-solid denser liquid called "Gel". In there we have a metal oxide creating metal as oxopolymer(M-O-M) or hydroxo polymers (M-OH-M). Now we heat the gel without string and after some higher temperature the burning agents burn to provide with a localized very high temperature which will break the chain further dehydrating and we have dried ashes of the sample.

3.2 Synthesis of BCTCV

Ca, V and Cu doped BaTiO3 with chemical formula $Ba_{(0.9)}Ca_{(0.1)}Ti_{(1-3x)}Cu_{(x)}V_{(2x)}O_3$ (x=0, 0.0046, 0.0093) written as BCTCV_1, BCTCV_2, BCTCV_3 are synthesized using Sol-Gel method. Solutions of Barium (II) nitrate (99.999%, Alfa Aesar), dihydroxybis (ammonium lactate) titanium (IV), 50% w/w aqua solution (Alfa Aesar), Calcium nitrate tetrahydrate (99.98%, metal basis, AlfaAesar), Copper(II) Oxide (99.7%, metal basis, Alfa Aesar) and Vanadium(V) Oxide (99.6%, Alfa Aesar) were prepared and the solutions were mixed and stirred vigorously for homogeneous mixing. A solution of citric acid (gelling agent) and ethylene glycol (burning agent) in a 1:1 molar ratio was added. The resultant solution was heated at 70 °C for 2 h with continuous stirring and then left at the same temperature until gel formation. The gel was burnt in the open air on the hot plate which yielded a fluffy powder. Ground powder was heated at 450°C for the removal of undesired nitrates and carbonates. The obtained powder was further ground and calcined in air for 6 hours at temperatures ~850 and 1100 °C. The powder was then pressed by a uniaxial hydraulic pressure into a 10 mm diameter pellet which was sintered at 1480 °C for 4 hours.



Figure 3.1: Sample preparation flow of BCTCV series using the sol-gel method

3.2.1 Calculations Involved

Targeted material here is $Ba_{(0.9)}Ca_{(0.1)}Ti_{(1-3x)}Cu_{(x)}V_{(2x)}O_3$ with x=0,0.0046,0.0093.the atomic mass of the quantity refers to the mass of 1-mole material. The atomic mass of Ba, Ca, Ti, Cu, and V are 137.325gm, 40.078gm, 47.8657gm, 63.56gm, and 50.94gm respectively.

The atomic mass of Barium Nitrate, Ba(NO₃)₂=261.35 gm

The atomic mass of Calcium Nitrate, Ca(NO₃)₂ =232.59 gm

The atomic mass of Copper Nitrate, CuO = 79.545gm

The atomic mass of Vanadium Pentoxide, V₂O₅ =181.88 gm

The atomic mass of dihydroxybis (ammonium lactate) titanium (IV)=298.0815 gm

Now the value of the material to be used to achieve the desired material is given by the formula;

M= (mass of the constituting material \times portion in the targeted formula \times mass of the targeted yield)/(Targeted mass)

Here the mass of targeted yield is 4 gm. Mass of the constituent material is the atomic mass of each constituent material. A portion is calculated after applying the value of x in the targeted equation and targeted mass is the mass of targeted material after applying the value of x in it and inserting the values of the atomic mass of Ba, Ca, Ti, V, Cu. In calculation, we have multiplied 2 in the case of Talh as it is a 50-50 aqua solution. The following table represents all the calculated value of materials used to synthesis targeted materials.

Sr.	Х	1-3x	Ba(0.9)Ca(0.					
No.			1)Ti(1-					
			$_{3x)}Cu_{(x)}V_{(2)}$					
			x)O3	Ba-nit	Talh	Ca-nit	V2O5	CuO
0	0	1	223.4661	4.2103	10.5279	0.4227	0	0
1	0.0046	0.986	223.5671	4.2084	10.3770	0.4225	0.0150	0.0066
2	0.0093	0.972	223.6682	4.2065	10.2263	0.4223	0.0301	0.0132

Table 3.1: Calculation table for synthesizing $Ba_{(0.9)}Ca_{(0.1)}Ti_{(1-3x)}Cu_{(x)}V_{(2x)}O_3$ with x=0,0.0046,0.0093.

3.3 Synthesis of BBC

Bi and Cu dopes BaTiO3 with chemical formula $Ba_{(1-x)}Bi_xTi_{(1-x)}Cu_xO_3$ (x=0,0.016,0.0312) written as BBC_1,BBC_2,BBC_3 are also synthesized using Sol-Gel method. Precursors used in this process are Barium (II) nitrate (99.999%, Alfa Aesar), dihydroxybis (ammonium lactate) titanium (IV) 50% w/w aqua solution (Alfa Aesar), Bismuth(III) Nitrate pentahydrate (98%,Alfa Aesar) and Copper(II)Oxide (99.7%, metal basis, Alfa Aesar). The rest of the preparation is the same as

previously. The sintering temperature is different depending upon Cu% ranging from 1350 to 1100 $^{\circ}$ C.



Figure 3.2: sample preparation flow for BBC series using the Sol-Gel method.

3.3.1 Calculations Involved

Targeted composition here is $Ba_{(1-x)}Bi_xTi_{(1-x)}Cu_xO_3$ with x=0,0.016,0.0312. All the material used, and their atomic masses are given as Atomic mass of Ba, Bi, Ti, and Cu are 137.325gm,208.9804gm 47.8657gm and 63.56gm respectively.

The atomic mass of Barium Nitrate, Ba(NO₃)₂ =261.35 gm

The atomic mass of Bismuth Nitrate, Bi(NO₃)₂ =485.07 gm

The atomic mass of Copper Nitrate, CuO = 79.545gm

The atomic mass of Vanadium Pentoxide, V₂O₅ =181.88 gm

The atomic mass of dihydroxybis (ammonium lactate) titanium (IV)=298.0815 gm

All the other procedure of calculation remains the same as the previous series. Following the targeted material the values of constitute material used is been calculated as.

			Ba(1-					
Sr.			x)Bi(x)Ti(1-					
no.	х	1-x	x)Cu(x)O3	Ba-nit	Talh	CuO	Bi-Nit	Ba-nit
0	0	1	233.191	5.6037	12.6111	0	0	5.6038
1	0.0156	0.9843	234.5555688	5.4841	12.3418	0.0265	0.0871	5.4841
2	0.0312	0.9687	235.9201375	5.3659	12.0757	0.0527	0.1731	5.3659

Table 3.2: Calculation table for synthesizing $Ba_{(1-x)}Bi_xTi_{(1-x)}Cu_xO_3$ with x=0,0.016,0.0312.

Chapter-4

Experimental Techniques

4.1 X-Ray Diffraction

4.1.1 Introduction

X-ray is a part of electromagnetic radiation which is very important to the scientific community. It was discovered by German physicist W.C. Rontgen on November 8,1895. He dedicated "X" in the name as an unknown. after him, P.P. Ewald studies them and in 1912 developed the formula to describe the transit of light through an ordered array of scattering atoms assuming crystal were made of "space-lattice" like construction. In that same year, von Laue published the first Diffraction pattern. It's a very powerful technique to study the composition and physical properties of the material such as strain, grain size, phase composition. Liquids and gases are non-crystalline while solid are found in crystalline and amorphous both. Amorphous materials are randomly situated in the system whereas solids materials have properly arranged atom. Due to this fact, we get constructive interference in the crystalline structures. In the consecutive year Bragg solve the first crystal structure of NaCl using a special case of Laue's diffraction. X-ray diffraction is centered on crystalline structures it does not mean it gives no information about amorphous material. Solid Material has 7 types of symmetry which given in table 4.1. The unit cell is the building block of material, basic repeating of a unit cell to make the whole material, it has all the symmetry elements to uniquely define the material. The key feature that the wavelength of X-ray is similar to the distance between atomic planes, we use X-ray in studying atomic structure. Each electron in atom scatter the light coherently and since the crystal is a periodic arrangement of those atoms, they produce diffraction.

Serial	Crystal class	Unit cell	Unit cell angles	Bravais
No.		Dimensions		lattices (P, C,
				I, F)
1	Cubic	a=b=c	$\alpha = \beta = \gamma = 90$	P, I, F
2	Tetragonal	a=b≠c	$\alpha = \beta = \gamma = 90$	P, I
3	Orthorhombic	a≠b≠c	$\alpha = \beta = \gamma = 90$	P, C, I, F
4	Rhombohedral	a=b=c	$\alpha = \beta = \gamma \neq 90$	Р
5	Hexagonal	a=b≠c	$\alpha = \beta = 90, \gamma$	Р
			= 120	
6	Monoclinic	a≠b≠c	$\alpha = \gamma = 90, \beta$	P, C
			≠ 90	
7	Triclinic	a≠b≠c	$\alpha \neq \beta \neq \gamma \neq 90$	Р

Table 4.1: The crystal structure and lattice parameters.



Figure 4.1: Unit cell diagram of a crystal with all lattice parameters.

Here P, C, I, F stand for Primitive unit cell, Base-centered, Body-Centered, and Face-Centered respectively. An schematic unit cell is drawn in Fig 4.1 to understand the lattice parameters and their respective positions to each other.

4.1.2 Principle (Miler Indices & Bragg's law)

The Miller Indices is used to specify planes and direction, these directions and planes could be off in lattices and crystals. they are given by h, k, l where (hkl) meaning plane, {hkl} represent family of planes,[hkl] direction from the origin,<hkl> family of direction. For 1-D lattice, there will be one miller indices and for 2-D there will be two. Vector $\vec{R} = a\hat{a} + b\hat{b} + c\hat{c}$ from origin to any lattice point is given as here a, b, and c are the length of basis vectors. Now if any planes cut the basis vectors at point h', k', l' then the value of a/h', b/k'and c/l' are equal to h, k, and l respectively.

h: k: l =
$$\frac{a}{h'}$$
: $\frac{b}{k'}$: $\frac{c}{l'}$

planes (110),(220), (330) are from the same family of planes denoted as {110}. The inter planar distance between two planes(d) is given by:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

Here h, k, l is the miller indices and a, b, c is the unit cell lengths. It's dependent on interference by diffracted wave by crystalline structure. It's used to check the structure and phase of the material. When a ray of wavelength comparable to the crystal length falls on the crystal structure it gets reflected from two planes which are d distance apart from each other and constructive interference to take place difference of path traveled by both rays should be an integral multiple of the wavelength of the incident spectrum. Path differences are given by $2 d \sin \theta$ (Fig. 4.2), This diffraction is given by Bragg's law; $2d \sin \theta = n\lambda$



Figure 4.2: Ray Diagram for the Bragg's Diffraction law.

Rearranging the two-equation we'll get.

$$\sin^2 \theta = \frac{n^2 \lambda^2}{4} \left(\frac{a^2 + b^2 + c^2}{h^2 + k^2 + l^2} \right)$$

n is the order of scattering, λ is the wavelength of the incident radiation, θ is the scattering angle. The overall effect from all of the plane families intensifies the diffraction at this point where Bragg's Law satisfies. these planes are called Bragg peaks. If we apply radiation in a range of scattering angles, we'll find a graph of different intensities at different angles by the in interplanar distances, which will be different for every symmetry of element.

4.1.3 Instrumental

The machine used to measure X-ray diffraction is called a diffractometer. There are 3 main parts of any Diffractometer.

- X-ray source tube
- Detector
- Goniometer

When an accelerated electron is bombarded on metal, they transform their energy and kick out to electron sitting in inner shells and another electron from other shell come to take its place, radiating X-rays. We apply a high voltage between the cathode and metal anode as the electron from cathode releases, they hit the target metal with kinetic energy most of it was waste in thermal energy (so the metal has to be cool all the time), but a fair amount is used to create X-rays. We can use all kinds of target material as anode like Mo, Cu, Co, Fe, Cr. They have wavelengths of 0.17Å, 1.54Å, 1.79Å, 1.94Å, and 2.29Å respectively. We can also use them according to our samples .The Cu is the most widely used, but samples that are rich in Fe, Cr, Mn will fluoresce under the incident Cu K_{α} beam and create polychromatic radiation. Exactly what you don't want. It can lead to strange shaped and elevated backgrounds. Diffractometers with Cu and Co targets are most popular as they produce wavelengths that can cover most of the crystalline structures. Cu target X-rays are produced in continuous wavelengths in which two wavelengths K_{α} and K_{β} have a higher intensity we apply optical filters and metal slits to collimate monochromatic X-ray radiation. That collimated radiation will now fall on the specimen which is placed on Goniometer which was used for holding and moving the sample. X-rays after diffracted by the sample, Diffracted X-rays first passes through slits and then through monochromatic filters before going to the detector to suppress any other wavelengths. The detector measures the count of photons that are coming at every specific scattering angle. It does that by two means:

(1). θ : θ arrangement: in this configuration samples remains stationary and X-ray tube and detector rotate to get the readings. As shown in Fig.4.3

(2). θ : θ 2 arrangement: In this configuration X-ray tube remains stationary and the sample holder and detector rotate to get the readings.



Figure 4.3: Schematic diagram of X-Ray Diffractometer in $\theta:\theta$ geometry.

In our experiment, we have used Bruker D2-Phaser Diffractometer with Cu anode, which produces an X-ray of wavelength~1.5406 Å. We have recorded the data in limit $20 < 2\theta < 80$. Which is been shown in Figure 4.4.



4.2. Raman Spectroscopy

4.2.1 Introduction

It works on the principle Raman effect in Molecules proposed by Indian Scientist Sir ChandrasekharaVenkata Raman in 1928. It's a very weak effect only 1 out of one million scattered light particle or photon exhibits this effect. Raman spectroscopy is a very efficient way to study the system when X-ray diffraction gives information about a certain plane in the system, Raman spectroscopy provides information about short-range ordering. It is more sensitive with comparison to X-ray diffraction in the crystal structure, phase transition, defects, stoichiometry, strain, etc. as it focuses on the local symmetry of the system and phonon modes are profoundly adjusted with unobtrusive change bond length and strains and so on. It is utilized to observe vibrational, rotational, and low-frequency phonon modes in the material. When a photon of light interacts inelastically with Vibrating molecules it gives Raman effect, Due to this interaction the energy of emitted light changes and it gives information about the system.

4.2.2 Principle

When the light of energy and frequency is bombarded on any sample, the energy of a photon can be absorbed by a molecule and can go to any excited state momentarily when it returns to the original state it emits a photon of the same frequency and energy, this is called elastic scattering (Rayleigh scattering). However sometimes they do not come back to the original states from which they were excited, this is called inelastic scattering (Raman scattering). When they return to a lower energy level from where they were excited they take energy from the photon and emitted photon will have more energy and frequency, this is called "Anti-Stokes spectrum" and when they come from an excited state to a state with higher energy level from where they were excited they give extra energy to the emitting photon, so emitted photon now have less energy and frequency, this is called "Stokes-Spectrum". A general explanatory diagram is drawn in figure 4.5.



Figure 4.5: Principle of Raman scattering

Although in general, we see more of the stokes spectrum than to antistokes spectrum because for anti-stokes spectrum to happen molecules have to be excited before the interaction which is very unlikely to happen at room temperature. So, in the emitted spectrum you will get maximum Rayleigh then stokes and then anti-stokes spectrum in terms of intensity $I_R>I_S>I_AS$. So, we conventionally measure the stokes spectrum to study the material whereas in the case of fluorescing molecules we use the antistoke spectrum as a stoke spectrum that causes interference with fluorescing molecules. Raman scattering is dependent on the incident wavelength whereas its magnitude is not dependent on incident wavelength, magnitude depends upon how vibrational modes respond to the applied energy, every vibrational mode requires certain energy to get excited and this is what segregates each molecule's Raman responses. Raman spectrum is recorded as an intensity Vs Raman shift graph.

4.2.3 Instrumentation

To study the Raman effect the machine used is called Raman spectrometer it has a few main components that are necessary for every spectrometer from very basic to very advance. These components are:

- Laser
- Filter and microscope
- CCD detector and recording system

The first thing in any spectrophotometer is a source of radiation, in our case which is a laser. It is used to excite the molecules, there are different types of laser available such as Argon-ion laser (488 and 514.5nm) Krypton ion laser (530.9 and 647.1 nm), Helium-Neon laser (632.8 nm) Near Infrared (IR) diode laser (785 and 830 nm). It is to be considered that low wavelength laser with such high energy will cause large fluorescence and cause permanent damage to the sample(photodecomposition). Once a suitable laser is been selected, we proceed further via first pointing laser to a preferred target in the sample with the help of normal mirrors and folding mirrors and microscope. After that, since the incident and scattered light have the most same wavelength and the difference between intensities of Rayleigh scattered spectra and Raman spectra are very large, Notch filters and band pass filters are used to separate Raman spectra from total reflected spectra .now detectors are used to disperse the Raman spectra into its constituent parts generally it is a Charge Coupled Device (CCD) photo detector. With the help of recording system, data is displayed on the screen as an Intensity Vs Raman shift graph. A Schmitt diagram of all the constituent parts and spectrometer is given below in the Fig. 4.6.In our experiment, we have used Horiba company's LabRAM HR Evolution Raman spectrometer(Spectral resolution of 0.9 cm⁻¹)Fig.4.7. A He-Ne laser was used in the excitation of molecules with wavelength 632.8 nm. With the help of LabRAM software, we can use a computercontrolled scan range, integration time, scan speed, repetition of the scan, laser power and many more to optimize the error and get the most accurate result of our samples.



Figure 4.6: Schematic diagram of Raman spectroscopy [ref:<u>https://commons.wikimedia.org/wiki/File:Setup_Raman_Spectroscopy_ada</u> <u>pted_from_Thomas_Schmid_and_Petra_Dariz_in_Heritage_2(2)_(2019)_1662-</u>

1683.png]



Figure 4.7: Horiba LabRam HR Raman spectrometer.[ref:<u>https://www.horiba.com/en_en/products/detail/action/sho</u> <u>w/Product/labram-hr-evolution-1083/]</u>

4.3 UV-Vis Absorption Spectroscopy

4.3.1 Introduction

When electromagnetic radiation interacts with material, several things are happening such as reflection, absorption, transmittance, Scattering. These processes happen all around us on a daily basis, however, if we study them, they can provide information on the sample. For example, Red ball appears us to be red while shine by a white light because it absorbed all the other wavelengths of the incident radiation and only red color it reflected. The same way all the light on glasses are transmitted since incident radiation does not have enough energy to excite electrons of SiO_2 in the glass so, they do not absorb any radiation and let the light pass away through them. Mainly there are two kinds of Reflectance named as Specular reflectance and Diffused reflectance as shown in Fig.4.8.



Figure 4.8: Schematic of Specular and Diffuse reflection

• **Specular:** It is also called "mirror-like" reflection, When radiation in an incident on the perfectly ordered interface and they have an imperfection in order less than the wavelength of the incident light, the reflected light angle will be same as incident light angle and reflected light will go in a straight line and most of the light is been reflected in this case such as Polished metal surfaces, glass, liquid surfaces.

• **Diffused:** When the order of imperfection is larger than the incident radiation the radiation gets reflected in many directions and there is more absorption in this case. Fig comparing both

Diffused reflection is used in UV visible and Near Infrared(NIR) spectroscopy.

4.3.2 Principle

When radiation of intensity is incident on a surface of some width and it absorbs some part of intensity and transmits remaining, the relation between the incident and transmitted radiation is given by Beer-Lambert law:

$$I = I_0 e^{-\alpha t}$$

here α is the coefficient of absorption, given as (for t=1)

$$\alpha = -\ln\left(\frac{1}{10}\right),\,$$

Absorption light intensity is the difference between incident and transmitted light intensity. the ratio of transmitted light intensity to the incident light intensity is:

$$T = \frac{I}{I_o}$$

Here T, I_0 ,I,t are called Transmittance of the material, incident intensity, transmitted intensity, and width of the sample respectably at a particular wavelength. T=1 for a purely transmitted sample. Similarly, for diffuse reflective sample the ratio of reflected light intensity to incident light intensity is:

$$R_{\infty} = \frac{J}{I_0}$$

Here R_{∞} , J is called absolute remittance and reflected light intensity. Subscript ∞ refers to the fact that in absolute remittance we have considered the sample to be infinitely thick so all that there is no transmittance and incident light never penetrates to sample holder[Rahul thesis]. since this not the case always the quantity we measure is called relative remittance which is

$$R'_{\infty} = \frac{R_{\infty sample}}{R_{\infty standard}}$$

For and reflected sample $R_{\infty standard}=1$ and $R'_{\infty}=R_{\infty sample}$. In the case of transmittance, it is always convenient to represent data in the absorption unit as absorption is linearly proportional to absorbing material according to Beer's law. Beer's law gives the relation between the absorption coefficient and the transmittance of the material

$$\alpha = \ln\left(\frac{1}{T_0}\right)$$

Diffuse reflectance spectroscopy (DRS) is used to obtain Bandgap of powder sample as they scattered in a perfectly diffused manner. It follows on Kubelka-Munk theory who gave a similar function for diffusive reflectance as:

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{K}{S} = \frac{2.303C\varepsilon}{S}$$

Here $F(R_{\infty}), R_{\infty}$, K, S, C, ε , S are Kubelka-Munk function, percentage of reflectance of material, absorption Coefficient, S is twice the scattering Coefficient of material, C is analyte concentration and ε is absorptivity respectively. Here K is twice the Beer's Law absorption coefficient.

Kubelka-Munk function is proportional to the absorption coefficient now the above equation can be written as:

$$F(R_{\infty}) \propto \alpha \propto \frac{(hv - Eg)^{1/n}}{hv} \Rightarrow (\alpha hv)^n = A(hv - E_g)$$

Hereh,v, Eg, A, and n are plank constant, frequency of incident radiation, Bandgap of material, the proportionality constant, and the quantity which lets about the nature of the transition. n=2 for direct allowed transitions. Tauc et al. proposed to estimate the bandgap of samples from absorption data using Bloch theorem[47]. Davis and Mott enhanced it for all material and concluded that a plot of $(\alpha hv)^n$ vs (hv) can find a linear region which will be used to find the bandgap, Eg[48].The graph where we plot $(\alpha hv)^n$ VS (hv) is called the Tauc Plot. This graph will be of state line such as, y=mx+c. after linearly fitting it for a strain line, we'll get the value of slope and intercept, the ratio of intercept to the slope will give us the bandgap of the system. The data of reflectance can also be used to calculate the Urbach energy (E_u) of the sample which essentially tells about the degree of structural disordering or poor crystallinity in the sample. E_U can be calculated from the slope of a logarithmic plot of ln[α] and hv as[49];

$$\ln[\alpha] = \ln[\alpha_0] + \left[\frac{h\nu}{E_U}\right]$$

Here α , α_0 , h, ν and E_U are absorption coefficient, absorption constant, plank constant, frequency of the incident light, and Urbach energy respectively.

4.3.3 Instrumentation

The instrumentation key components are the same as any other spectrometer such as source, monochromator, beam splitter, sample holder, detector, signal processor, and readout. Here a Tungsten-halogen or Deuterium lamp is used as a source to create UV light in the range of 200nm to 1100 nm, radiation is passed through a monochromator to select a single wavelength then this radiation is passed through a beam splitter which divides is in two-part one part is sent directly to the detector and another part to the sample. The sample now absorbs some of the parts and reflects the rest of the part, which is now sent to another detector. The detector used is photodiode or CCD detectors. Now signal processors calculate reflectivity and save data of reflectivity for every hv value. A schematic diagram of the instrument is given in figure 4.9.



Figure 4.9: Schematic diagram of the UV-Vis spectrometer

After getting the data we plot the Tauc-plot and calculate the bandgap of the samples in our experiment we have used Research India's Spectra CCD detector in or work which was placed in a black box for light blockage.

4.4 Dielectric Spectroscopy

4.4.1 Introduction

Dielectric spectroscopy or impedance spectroscopy of material is been used to study the electric impedance, admittance as a function of the frequency of an applied signal. In dielectric microscopy, we use radio and microwave frequency in applied signals, so they interact with the material and we study the behavior of the dipolar reorientation mobility of molecules in the system. Dielectric spectroscopy also provides information on many material parameters such as complex permittivity and DC electrical conductivity of the system. It is also used for calculating dielectric properties such as dielectric constant and dielectric loss. Temperature and frequency-dependent Dielectric study is the most important technique to understand the phase transition behavior of any ceramic material. It is also used to study the behavior of the bound and space charge present in the bulk or interface region of any system.

4.4.2 Principle

as:

For only the resistive system current passing through the sample on applying a constant voltage, V is given by Ohm's law.

V = IR

Similarly, when an A.C. voltage is applied between any sample the current passing through the sample is then given as,

$$V = IZ$$

Here Z is called the impedance of the material which is an applied signal frequency-dependent quantity for purely resistive, capacitive and inductive system impedance of the system is given as:

$$Z_{L} = j\omega L$$
 $Z_{C} = \frac{1}{j\omega C}$

Voltage signal applied to the system is represented

$$V = V_0 \sin(\omega t)$$

Here V_0 is the magnitude of the applied voltage and ω is the angular frequency which can be written as, $\omega = 2\pi f$, where f is the frequency of the applied signal.

The response current in the system will be:

$$I = I_0 \sin(\omega t + \theta)$$

Here I_0 is the magnitude of the current, ω is the angular frequency and θ is the phase difference between the applied voltage and response current. This phase difference is dependent upon the reactance of the system. Now the Impedance of the system is given as:

$$Z = \frac{V}{I} = \frac{V_0 \sin(wt)}{I_0 \sin(wt + \theta)} = Z_0 \frac{\text{Imaginary part of } e^{(j\omega t)}}{\text{The imaginary part of } e^{j(\omega t + \theta)}} = \frac{Z_0}{e^{j\theta}}$$

Using Euler's equation for imaginary numbers;

This can be further be written as :

$$V = IZ = IZ_0 e^{(j\theta)} = Z' + jZ'' =$$

Here Z_0 is the magnitude of impedance, $j=\sqrt{-1}$ is the imaginary part, θ is the phase difference between applied voltage and response current, Z' is the real part of impedance which is due to resistive part of the sample and Z"the imaginary part of impedance which is due to the reactance of the sample. Plotting Z" on

Another property of tetragonal perovskites is a diffused type of phase transition that is exhibited by a broad peak instead of a sharp peak at T_m . pure BT is well-known for showing sharp tetragonal ferroelectric to cubic paraelectric transitions. It is expected that a solid solution of these materials will also show similar behavior. Diffused transitions occur when

a different type of atom sits at an identical site of the perovskite structure. Such a transition can be described by a modified Curie-Wiess law.

$$\left(\frac{1}{\epsilon} - \frac{1}{\epsilon_{m}}\right) = \frac{(T - T_{m})^{\gamma}}{C}$$

where ε_m is the dielectric constant (maxima) at Tm, γ ($1 \le \gamma \le 2$) is the degree of diffuseness, and C is Curie-Wiess constant. γ ($1 \le \gamma \le 2$) is a degree of diffuseness and C is Curie-Wiess constant. For purely ferroelectric material, $\gamma=1$ and a relaxor $\gamma=2$. A linear fit of $\ln(\frac{1}{\epsilon}-\frac{1}{\epsilon_m})$ vs ln (T – T_m) plot at a fixed frequency provides an estimation of γ .

4.4.3 Instrumental

We have used Newton's 4th LTD PSM 1735 phasesensitive to measure the parallel capacitance (C_p) and tan delta of the sample Figure 4.10. Here sample is been placed in parallel capacitor configuration with circular disk electrodes were made by silver pasting both faces, its diameter and thickness is been measured and then it is placed inside a sample holder which is a brass cylinder with copper contacts now this sample is placed between these cylinders and copper wire is used to connect contacts with an instrument which is then placed inside furnace where the temperature of the furnace is been controlled with a PID controller with an accuracy of 0.1°C. the controller is attached to Newton's 4th LTD PSM 1735 phase-sensitive (Figure 4.10) which will measure Parallel capacitance and tan delta as a function of temperature and frequency. We apply a potential of 2V peak to peak voltage with increasing frequency to the sample.


Figure 4.10: Newton's 4th LTD PSM 1735 phase-sensitive for dielectric measurements.[ref:<u>https://www.newtons4th.com/products/frequency-</u>response-analyzers/psm1735-frequency-response-analyzer/]

4.5 PE hysteresis loop

4.5.1 Introduction

As we know the basic difference between any material and ferroelectric material is that in ferroelectric material the direction of permanent electric polarization can be reversed permanently by applying an electric field once, hence they exhibit a hysteresis loop. when applied by an oscillating electric field. These properties of ferroelectric material have many applications as data storage devices and many more. The area enclosed by the PE loop is referred as energy loss in ferroelectric material.

4.5.2 Principle

PE hysteresis loop measurements is been carried out using the sawyer tower circuit. The circuit diagram of the sawyer tower circuit is given below in figure 4.11.



Figure 4.11: schematic diagram of PE loop tracer.

Here we have two capacitor one is due to the sample and one is the reference capacitor both of them are in series and value of C_x is chosen very high in comparison to C_{sample} to get greater potential difference at C_{sample} So that voltage drop across C_{sample} is nearly equal to the applied voltage. Now we give these signals to CRO to trace the polarization VS electric field graph. There are many kinds of Polarization Vs electric field graph is been reported, not all of them represent actual ferroelectric behavior. Mahesh peddigari have explained schematically how the PE hysteresis loop for dipole domains would look like in a particular structure [51].



Figure 4.12: PE loop variation with dipole domain alignment.[Ref.51]

Current density is given at the derivative of polarization to the electric field. The graph in which the value of current density maxima is at the same value with Coercive electric field and current density minima is at the same value with remnant polarization. Those materials are very close approximations of a pure ferroelectric material. Another graph is of relaxor type ferroelectric material [50].

4.5.3 Instrumental

We have used Marine India's PE loop tracer (Fig. 4.13) for the hysteresis loop measurements. At first circular sintered pellets were polished, and silver pasted on the face to make electrode, we'll use silicon oil heated and then cooled to prevent sparking from the edge of the sample due to very high voltage. We heated the oil at first to prevent any air bobble in the oil. We have placed the sample in the sample holder, submerged is in the silicon oil and start to increase the value of applied voltage with fixed frequency across the sample which will create electric filed according to the thickness of the material. The figure of the used instrument is given below.



Figure 4.13: Marine India PE loop tracer and schematic diagram of measurement setup

[Ref;http://www.marineindia.com/pe%20loop%20tracer%20.html]

4.6 FESEM(Field emission secondary electron microscopy)

4.6.1 Introduction

Scanning electron microscopy is a technique used to do the advance study of the surface properties, where instead of light, the electron is been used to see the morphology of samples. As compared to the optical microscope this helps to observe the surface morphology at higher resolution, higher magnification, and at larger extent of focus. Because electrons have wavelengths very low compared to that of light, they can provide better resolution instead of optical microscopes. Dr. Ernst Ruska assembled the first electron microscope in 1931 and received a Nobel prize for physics in 1986 for that. We differentiate microscopes on the bases of how the electron is generated and the way they interact with the material. FESEM is one kind of Scanning Electron microscope, in SEM we use heat Tungsten wire to a very high temperature to remove the electron from material and then focuses it on the material whereas in FESEM a fine Sharp single cristal Tungsten tip is used in field emission Gun to eject electrons, where we use high voltage gradient instead of high temperature. The electron which examines the surface of the sample step by step is listed as a scanning microscope and the electron which goes through the samples shows an internal structure is called the transmission microscope.

4.6.2 Principle

Electron microscopy works on the principle that magnetic and electric fields can be used to converge or diverge the electron beam in the same fashion lenses do for light. The incident beam of electrons is produced from the field emission cathode penetrates through the specimen surface. Here, the number of interactions takes place producing backscattered electrons, transmitting electrons, secondary electrons, Auger electron, X-ray, etc. The energy of incident electrons varies from 100 eV to 30 KeV. The surface electrons escaped from the sample surface are affected by the incident electrons interact with the sample surface and the near-surface, it may be an elastic collision or inelastic collision. If the elastic collision of incident electrons takes place with the nucleus of the sample atom, then high energy electrons are emitted knows as backscattering electrons (BSE) while if this collision is inelastic then lower energy electrons are emitted known as secondary electrons (SE) which if of energy 50eV or less. Velocity and angle of deflected secondary electrons are highly dependent on the structure of the sample, the microstructure sample information is got from the scattered secondary electrons later used in the formation of an image. As electron being a light matter, it will get scattered with anything in its path, so instrumental columns should be vacuumed.

4.6.3 Instrumental

We have used Supra-55 Zeiss-FESEM (Figure 4.14) in our work. In recording the morphology of the sample using SEM we need the following elements.

• Preparation

When accelerated electron beams are bombarded on the sample, some of the electrons embedded into the sample or on the surface of the sample, If the sample is not conducting, these electrons will charge the sample and when the charge is big enough, it will affect the incoming electron beam and change the trajectory of the incoming beam, these accumulated charges also affect the number of secondary electron making and therefore, increase the signal to noise ratio, making the image blurred or sometimes disappeared. To prevent this to happen we coat the samples with a thin layer of Conducting materials such as Gold(Au), Gold/palladium(Au/Pd), Platinum(Pt), Silver(Ag), etc. using a lowpressure sputter coater with the thickness of range 2-20 nm.

• Source of electron

The generation of the electron beam is the first step to any electron microscope.generally, a tungsten filament heated to a very high temperature (~2800°C) to create an electron beam, But in FESEM we use a "cold" source. An extremely sharp and thin tungsten needle is used as a cathode and two anodes are used named as primary and secondary anodes, to reach a better point to point resolution. a voltage of range 0.5-30 kV is applied between electrodes to create the electron beam. Electron beam created by field emission is ~1000 times(3to 6 times better than SEM) smaller than a standard microscope, it gives higher resolution.

• A column with lenses and aperture

The electron beam is focused on a tiny sharp point using electromagnetic lenses(condenser lens, scan coil, objective lens, Stigmator coil)

Condenser lens

The first lens in the column is the condenser lens, coming from the source the electron beam pass through the condenser lens, the main purpose of this lens is to control the diameter of the electron beam. A narrow beam will increase the resolution but also increase the signal to noise ration. It consists of two parts.

Scan coil

Scan coil scan the sample by the zig-zag motion of an electron by the coil. The image that you see on the monitor has a scan speed, which is the speed of the deflected electrons on the sample by scan coil.

The objective lens

It's the last lens on the column, it focuses the electron beam on the sample. The distance between the objective lens and the sample should be appropriate so that the objective lens does not have to apply greater force to deflect the electron beam to the sample.

Stigmata coils

These coils are used to make sure that the electron beam incident on the sample is perfectly circular. If the beam is something like ellipsoid the image is blurred and looks like stretched on one axis.

A Schmitt diagram of the column is given here for references in figure 4.14.



Figure 4.14: schematic diagram of the FESEM .[ref: <u>https://www.researchgate.net/figure/Schematic-diagram-of-Field-</u> <u>Emission-Scanning-Electron-Microscope-FESEM_fig31_318487306</u>]

Object chamber

After samples is been coated it is placed on a sample holder which is then placed in a vacuumed chamber. It is placed on a movable and rotating stage. Many samples can be placed on the stage(~9) at once so that you don't have to ventilate and vacuum the chamber for each sample. The stage can be operated by a controller, sitting outside, with which you can change the position in X, Y position, and can also rotate the stage the and one real-time camera is also present in the chamber to see the positioning of the sample.

Image formation

When the primary electron is bombarded on the sample, they create a secondary electron of different velocities and angles according to the surface morphology of the sample. Now, these secondary electrons hit the detector, which is having a layer of the scintillator, which a fluorescence material. Now, these signals that the scintillator produces will be amplified and transduced to the video signal. This signal is directed to the screen of the monitor and a real-time scanned image is shown on the screen.



Figure 4.15: (1) Image of Supra55 Zeiss-FESEM used in our work, (2) computer screen to see live video signal, (3) Inca software attached within

the computer for EDX and elementary mapping and (4) and (5) Gold coating set up.

Chapter-5

Results and Discussion

In the following chapter, we'll discuss all the results we have got from the various experiments. We'll first discuss the structural properties and after that vibrational, optical, morphological, and dielectric response for both of our synthesized series BCTCV and BBC. After that, we have also done PE hysteresis loop analysis for all the samples to understand the change in the electric field responses with doping in the samples.

5.1 Structural properties

To verify the structure and for phase identification of these materials, X-ray diffraction was performed by a powder X-ray diffractometer (Bruker D2 Phaser X-ray diffractometer) with Cu K α radiation ($\lambda = 1.5406$ Å). The spectra were recorded in the 2 θ range, 20° - 80° in the step size of 0.02, where the rotational speed of X-ray tube with respect to the detector was 1° per minute for both series since the diffractometer is in θ : θ arrangement.

5.1.1 X-ray diffraction for BBC

In the Bi and Cu doped BaTiO₃, X-ray diffraction pattern reveals that all the samples are crystalline, The pattern shows pure tetragonal phase with (*P4mm*) space group (Fig. 5.1). Here also we are having a double peak at approx. 45° and there is no change in the shape of the peak. With an increase in doping concentration the peaks are shifting towards the higher 2θ value.



Figure 5.1: X-ray diffraction pattern of BBC series.

Again, the phase identification was done using Fullprof software suit. All the samples are found to be in a pure tetragonal phase. A comparison between the refined data and observed data of the second sample is shown here if Figure 5.2.



Figure 5.2: profile matching of BBC.

The lattice parameters are calculated by profile matching using Fullprof software suit. Variation of lattice parameters and cell volume are also shown. Lattice parameter 'a' decreases and 'c' increases at doping concentration x=0.015 and the trend reverses slightly with further increase in doping concentration at x=0.031. Such variation in lattice parameters results in increase in tetragonality (defined by (c/a) ratio) of the material as shown in inset of Fig 5.3. When a smaller ion replaces Ti⁴⁺, the cell becomes smaller; resulting in the distance between Ti and O becomes shorter. This enhances the interaction between these ions, which may results in decrease in lattice parameters. When an ion with less electric charge replaces Ti⁴⁺, the coulomb interaction between O²⁻ and the cation in B-site is weakened, which may result in elongation in lattice parameters. The extra charge of Bi³⁺ also helps in charge neutralization of the lattice. The competetative nature of small ionic size and small charge may be reason behind such variation of lattice paramters in the system. Tetragonality in the doped system first increases with doping and with further addition of dopant element the tetragonlity decreases. This result is in agreement with previous report.



Figure 5.3: (A) lattice parameters, Tetragonality (c/a) and (B) Unit cell volume with doping concentration in BBC series.

5.1.2 X-ray diffraction for BCTCV

X-ray diffraction (XRD) pattern of the prepared samples are taken after grinding the sintered pellets. X-ray diffraction patterns of BCTCV1, BCTCV2, and BCTCV3 are shown in Fig. 5.4. The patterns reveal a crystalline phase of the prepared materials with the presence of very small peaks of BaTi₂O₅ near 30°, of the 2 θ value. All the samples have a double peak at around 45°-46° which is said to be the indicator for a tetragonal symmetry. Here this peak is becoming less sharp and another small peak is emerging in between two main peaks with the doping concentration which indicates that another phase may appear and the tetragonality of the sample will decrease with doping concentration.



Figure 5.4: X-ray diffraction patterns of the BCTCV series.

Later the spectra were analyzed using Fullprof software suit and profile matching is done to check the phase of the sample. It is found that the only

Ca doped sample is in pure tetragonal phase. The refinement of the Ca doped material is shown here in Figure 5.5. Here all the peaks were perfectly matched with the tetragonal phase and the value of $\text{Chi}^2 \sim 3$.



Figure 5.5: profile matching of Ba_{0.9}Ca_{0.1}TiO₃ using Fullprof software suite.

Whereas in the remaining sample the peaks were not matching with the tetragonal structure possibly because of another phase coexisting with the tetragonal phase in these samples and the samples were becoming less tetragonal with the doping concentration. The other phase has to be the next more asymmetric crystal structure possible because with doping we are increasing impurities and asymmetry in the pure sample, in this case, which is orthorhombic structure. So, profile matching is done using double phase refinement. It shows a mixture of tetragonal and orthorhombic phases coexist in BCTCV_2 and BCTCV_3.Which is shown in figure 5.6.



Figure 5.6: Comparison of the single-phase refinement of Tetragonal and Orthorhombic phases with the mixed-phase refinement.

We can see that the XRD peaks are now well fitted with mixed-phase refinement. Lattice parameters of the samples were calculated with the help of Fullprof software suit and plotted against the doping concentrations in figure 5.7.



Figure 5.7: (A) Lattice parameters a and c with tetragonality (c/a) and (B) volume of the unit cell with doping concentration in BCTCV series.

BCTCV1 that contains Ca in BaTiO₃ is showing the tetragonal phase only. The presence of the orthorhombic phase is observed when doped with V and Cu, and the orthorhombic phase percentage increases with an increase in doping. In the tetragonal phase, the lattice parameter 'a' decreases, and 'c' increases increasing c/a ratio, and also here is an increase in unit cell volume with the doping concentration.

5.2 Vibrational Properties

The results obtained here are stokes spectra recorded by Horiba company's Lab-RAM HR Evolution Raman spectrometer(Spectral resolution of 0.9 cm⁻¹) and He-Ne laser was used for the excitation of molecules with wavelength 632.8 nm, here we have used only 10% of the power with the 10-sec acquisition. Raman spectra of any material are sensitive to local symmetry and provide information about short-range ordering. Five atoms per unit cell in BaTiO3 give fifteen degrees of freedom.[12].In the cubic phase, both the symmetry modes are Raman inactive. Hence, first-order Raman effects are absent in the cubic phase.[12] But in the tetragonal phase, all the optical modes are Raman active the cubic F1u symmetry modes split into tetragonal A1+ E symmetry modes while F2u split into B1 + E. The A1 modes correspond to lattice vibrations along the c-axis while the E modes correspond to lattice vibration in a (or b)-axis. Each of the A1 and E modes further splits into a pair of TO (transverse optical) and LO (longitudinal optical) modes because of long-range electrostatic force owing to the ionic properties of the lattice. Among these, E(LO + TO) + B1 modes (derived from cubic F2u) are degenerate and are also known as cubic silent modes.

5.2.1 Raman Spectroscopy for BBC

XRD measurement gives information about long range or static symmetry, while for short range ordering or local structure information can be obtained more precisely from Raman spectra. Fig. 5.8 shows the Raman spectrum of BBC1, BBC2 and BBC3 specimens. Raman shift peaks located at around 306.9, 517.7, and 718.5 cm⁻¹ of BBCT1 are well match with the typical Raman peaks of the tetragonal BaTiO3 phase. Lu et al. reported that the peak near 300 cm⁻¹ is reduced in its sharpness and becomes indistinct when the tetragonal phase is not dominant. Here all samples, the peak near 306.9 cm⁻¹ is more dominant and show sharpness

with high intensity is the indication of the existence of its tetragonal phase. The peak at 306.9 cm⁻¹ is a combination of [B1, E(TO + LO)] modes and its presence indicates the asymmetry of TiO₆octahedra within the BaTiO₃ structure .This mode is also known as silent mode. This mode softens with doping, but the rate of softening decreases with increase in doping concentration. In Pb doped BaTiO₃, this mode softens but the intensity and sharpness increases continuously, which is a sign of increase in tetragonality. In present case, although the mode softens, the sharpness of the mode also decreases with increase in doping concentration. Yet the tetragonality increases and tetragonal to cubic phase transition temperature increases as confirmed from Room temperature XRD and temperature dependent dielectric study. There are two different peaks, [A1(LO), E(LO)], very close to each other around 720 cm⁻¹, and in powder Raman mostly it appears as single peak. This peak is related to A-site defects in BaTiO₃. In present study it is observed that this mode soften slightly with doping of, where Ba^{2+} is replaced with Bi^{3+} . This softening can be described by the effective mass. Due to incorporation of Bi in place of Ba, the effective mass of A-site increases, as a result the vibrational mode shifts toward lower frequency. The asymmetry in the peak at 517.7 cm⁻¹ suggests the coexistence of coupling of TO modes associated with the tetragonal phase. The peak at 307 cm⁻¹wavenumber which corresponds to the modes due to change is octahedral is been shifted towards left. This kind of shift is referred to as red shift.

We have fitted all the available peaks by Fityk software using the Voigt function. One of the fitted data is been shown here in fig.5.9. Every peak corresponds to a specific vibrational mode which is measured as peaks. We have fitted the data using 11 peaks due to the fact, in a complex system such as $BaTiO_3$ generally few peaks couple together to give one peak. The highest intensity peak is the interference peak which is not due to specific vibrational mode but due to interference of two modes.



Figure 5.8: Raman Spectroscopy of BBC samples.



Figure 5.9: Peak fitted data of BBC1 Sample.

5.2.2 Raman Spectroscopy or BCTCV

Room temperature Raman spectroscopy results obtained from diffractometer are plotted here using origin8.5 pro software. The plotted data is given here in figure 5.10.The peak at 307 cm⁻¹ wavenumber, which corresponds to the modes due to change is octahedral is been shifted towards left. This kind of shift is referred to as red shift.



Figure 5.10 Raman Spectroscopy of BCTCV samples.

.We have fitted all the available peaks by Fityk software using Voigt function. One of the fitted data is been shown here in fig.5.11. Every peak corresponds to a specific vibrational mode which is measured as peaks. We have fitted the data using 11 peaks due to the fact, in a complex system such as $BaTiO_3$ generally few peaks couple together to give one peak. The highest intensity peak is the interference peak which is not due to specific vibrational mode but due to interference of two modes.



Figure 5.11: peak fitted data of BCTCV1.

5.3 Optical properties

Diffused reflectance spectroscopy is mainly used to calculate energy differences between the conduction and valence band of semiconducting materials. Urbach energy, which is related to disorder (higher entropy) and imperfection in the lattice, also can be calculated by diffused reflectance spectroscopy. So, with this, we'll find the bandgap as well as a comparative study of disorder, if any, in the synthesized samples.

5.3.1 UV-Vis spectroscopy for BBC

Along with very good ferroelectric properties, multifunctional BaTiO3 also shows semiconductive properties. To investigate the semiconductive behavior of the prepared samples, diffuse reflectance spectra (DRS) is recorded at room temperature. Kubelka-Munk function is calculated using the formula, $F(R) = \frac{(1-R)^2}{2R}$, where R is reflectivity of the powder used for experiment. Since F(R) is proportional to absorption coefficient, direct band gap is calculated by plotting the linear region in $(F(R)hv)^2$ vs hv plot. Data from the spectrometer is again used for Tauc-plot. And we calculated the value of bandgap and Urbach energy from these plots. Findings is been tabulated in table 5.1. and the corresponding graph is been plotted in figure 5.12.

Sr.	Doping	Band	Error in Band	Urbach	Error in Urbach
No.	concentration(%)	gap(eV)	gap(eV)	energy(meV)	energy(meV)
1	0	3.2609	0.09591	180.36054	0.72053
2	1.56	3.2076	0.09398	422.02996	3.90059
3	3.12	3.1695	0.06104	422.70787	4.87625

Table 5.1: Band gap and Urbach energy results for the BBC series.

the graph is been plotted to understand the effect changes in bandgap and Urbach energy. There is not much change in Bandgap, within the error limits, the bandgap is constant. Still, it shows a little decrement in the bandgap energy and Urbach energy is increasing with doping concentration meaning that the disorder in the sample increases with an increase in doping concentration.



Figure 5.12: (A) UV-Vis data of the BBC series with (B) band gap and Urbach energy results of the BBC samples.

5.3.2 UV-Vis spectroscopy for BCTCV

The data observed from the spectrometer is % reflectance concerning the applied energy hv from there we calculated Kubelka-Munk function from data and plotted Tauc-plot to calculate band direct bandgap of the synthesized series. We also calculated Urbach energy for the samples. The calculated data is been presented in table 5.2.

Sr.	Doping	Band	Error in Band	Urbach	Error in Urbach
no.	concentration(%)	gap(eV)	gap(eV)	energy(meV)	energy(meV)
1	0	3.274	0.0685	718.2	3.002
2	0.46	3.278	0.05026	777	3.13939
3	0.92	3.302	0.07355	779.76	3.0218

Table 5.2: Band gap and Urbach energy results for the BCTCV series.

Fig.5.13(A) reveals that there are not any significant changes in the bandgap energy with doping concentration but from Fig (B),the Urbach energy is increasing which tells us the disorder in the samples is increasing with doping.



Figure 5.13: (A) UV-Vis data of BCTCV series and (B) band gap and Urbach energy results of the BCTCV samples.

5.4 Dielectric Measurements

Study of temperature and frequency-dependent dielectric properties is one of the most effective tools to study phase transition behavior of materials to make samples in capacitor configuration electrodes were made by applying the silver paste on the faces the sintered circular disk of material. Later these were heated at 550°C for 10 minutes for removal of undesired chemicals. Dielectric properties including capacitance and dielectric loss were measured at different temperatures in the range of 50-300°C and different frequencies between 1 kHz and 1 MHz. Measurements were taken from Newton's 4th LTD PSM 1735 phase-sensitive, a 2 Volts peak to peak A.C. voltage is applied between electrodes. A phase transition from the tetragonal to cubic phases happens at a temperature, Tm, at which the dielectric constant is maximum. The tetragonal phase has a distortion related to the ferroelectric (FE) properties of the materials, which is absent in a cubic centrosymmetric phase. The cubic phase is dominantly paraelectric. We also measured the diffuseness of each material to check whether the material is working as a pure ferroelectric or diffused ferroelectric material.

5.4.1 Dielectric measurements for BBC

The second series BBC is also analyzed using room temperature dielectric measurements and plotted in Figure 5.14 Here the value of dielectric constant and dielectric loss(tan delta) is also decreasing continuously with increase in frequency but the value of the dielectric constant is decreasing with doping and loss is also decreasing with doping.



Figure 5.14: (A) Dielectric constant response with increasing frequency and (B) loss tangent response with increasing frequency for BBC series.

In the temperature-dependent study of the series the samples were analyzed with continuous temperature $(50-300^{\circ}C)$ and costume frequency in the range of 1000Hz to 20000Hz and is plotted in Fig.5.15(a)-(c).The value of change in transition temperatures also calculated for 10000Hzsignal frequency in table5.4. The maximum value of dielectric constant decreases with incorporation of dopant element. A phase transition from the tetragonal to cubic phases happens at a temperature, Tm, at which the dielectric constant is maximum. The tetragonal phase has a distortion related to the ferroelectric (FE) properties of the materials, which is absent in a cubic centrosymmetric phase. The cubic phase is dominantly paraelectric. In pure BT, this tetragonal to cubic phase transition takes places at ~ 128 C. In case of BBC1 (x=0.015), the transition temperature rises to 149 C. With further increase in dopant element (in BBC2), the Tc again decreases, yet higher than BT. It is reported that with further increase in doping of Bi and Cu, Tm decreases even more. Individual doping of both Bi and Cu lowers the Tc. Hence, codoping of these elements is the key factor for increase in Tc. The increase in c/a ratio (as observed from XRD) and increase in Tc is in agreement with each other.

Sr.no.	Doping concentration(%)	Transition temperature, Tc (°C)
1	0	128
2	1.56	146
3	3.12	140

Table 5.4: Change in the transition temperature concerning the doping concentration.

Tabulated data is plotted in fig.5.15(D). The cooperative effect of Bi^{3+} and Cu^{2+} may shorten the lattice in a-axis and elongate along c-axis, which results in increase in tetragonal strain. Thus more temperature is needed to attain the centro symmetric cubic structure in which all lattice parameters are equal. It is observed that loss factor (tan δ) increases with increase in doping concentration. The incorporation of Cu^{2+} may induce conductivity, as a result the loss factor increases. Here we have a high jump in the value of transition temperature; it is maximum for BBC2 and then decreases a bit but still is high compared to the pure BaTiO₃ sample.



Figure 5.15: temperature-dependent dielectric constant and loss tangent response in (A) BBC1,(B) BBC2 and (C) BBC3.(D) Change in Transition temperature of the sample with doping concentration.

In phase temperature dependent phase transition materials, there are two types of phase transitions: ferroelectric type and relaxor type. In ferroelectric type phase transition, there is a sharp peak in the temperature dependent dielectric constant. On the other hand, relaxor type materials show a broad peak over temperature range. To identify the type of transitions modified Curie-Wiess law: $\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T-T_m)^{\gamma}}{C}$ was used, where ε_m is the maximum dielectric constant at T_m and γ is diffusivity. For pure ferroelectric type phase transition, $\gamma = 1$. While for relaxor type of phase transition, $\gamma = 2$. The value of γ is estimated from the linear fit of $ln\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m}\right)$ vs $ln(T - T_m)$ (Fig 5.16). In all the samples, the value of γ are close to 1, which implies that all these materials shows ferroelectric type phase transition.



Figure 5.16:Modified Curie-Wiess law fitting $\ln(1/\epsilon - 1/\epsilon m)$ vs $\ln(T-Tm)$ and linear fitting (solid line) of the experimental data (symbols) of (A)BBC1, (B) BBC2 and (C) BBC3

5.4.2 Dielectric measurements for BCTCV

Dielectric measurements are been taken at room temperature with a continuous increase in frequency from 100Hz to 1M Hz. A continuous decrease in the dielectric constant and tan delta is been observed as we can see from the graph in figure5.17(A) and 5.17(B). Here the value of the dielectric constant is increasing and the value of dielectric loss (tan delta) is decreasing with doping which is most desired in any dielectric material.



Figure 5.17: (A) Dielectric constant response with increasing frequency and (B) loss tangent response with increasing frequency for BCTCV series.

After the room temperature dielectric study, we have studied the samples in a temperature-dependent environment with some custom frequencies ranging from 500Hz to 1MHz.Data is been recorded and plotted in Fig5.18 .The Main motive of the temperature-dependent study is to calculate transition temperature and find out the value of the maximum dielectric constant of the sample. The value of transition temperature and maximum dielectric constant with doping concentration is been recorded in table 5.4.for 10000 Hz signal frequency.

S.no.	Doping	Maximum Dielectric	Transition
	concentration(%)	constant (ϵ_m)	temperature, $T_c(^{\circ}C)$
1	0	1460.54749	131
2	0.46	1976.49174	134
3	0.92	2089.03649	131

Table 5.4: Maximum dielectric constant and transition temperature change with doping in the BCTCV series.

The variation in the transition temperature and maximum dielectric constant is plotted in figure (D) and (E) respectively. There is an increase in dielectric constant with doping, whereas transition temperature increases for BCTCV_2 and then again decreases for BCTCV_3.



Figure 5.18: temperature-dependent dielectric constant and loss tangent response in (A) BCTCV1,(B) BCTCV2, and (C) BCTCV3.(D). Change in Transition temperature of the sample with doping concentration and (E) change in the maximum dielectric constant of samples with doping concentration for 10000Hz frequency.

We have also calculated the value of the degree of diffuseness for all the samples from modified Curie-Weiss law and is been plotted in figure 5.19. The value of diffuseness is decreasing with doping, meaning the phase transition is becoming sharper at transition temperature and becoming more like ferroelectric than relaxor type transition.



Figure 5.19: Modified Curie-Wiess law fitting $\ln(1/\epsilon - 1/\epsilon m)$ vs $\ln(T-Tm)$ and linear fitting (solid line) of the experimental data (symbols) of (A)BCTCV1, (B) BCTCV2 and (C) BCTCV3.

5.5 PE hysteresis loop

RT ferroelectric property (polarization (P) vs electric field (E)) of Barium Titanate based ceramics is measured at frequency 50 Hz. A nonlinear conventional PE hysteresis loop and change in remnant polarization and coercive electric field with doping concentration are calculated.

5.5.1 Hysteresis loop for BCTCV

Polarization Vs electric field hysteresis loop is been studied. All the samples are performing hysteresis loop which has proper shapes. To further investigate the accuracy of the PE loop, the derivative of polarization concerning the electric field is plotted alongside the individual PE loop in Figure 5.20 (A)-(C). The first derivative of polarization dP/dE gives the rate of change of polarization with an applied electric field and is a measure of the capacitive properties of the material. The rate of change of polarization is maximum when most of the domains start to switch directions. A maximum in the dP/dE plot, hence, maybe closely related to mode switching inside the domain. Here maxima of the derivative are coinciding with E_c and minima with P_r , which further confirms the proper ferroelectric behavior hysteresis loop. The value of the Coercive field(E_c) and remnant polarization (P_r) is been calculated from the hysteresis loop and tabulated in table 44.

Sr. No.	Doping	Coercive	field,	Remnant Polarization,
	concentration(%)	2Ec(kV/cm)		$2Pr(\mu C/cm^2)$
1	0	8.82		8.18
2	0.463	9.58		9.06
3	0.926	14.17		15.66

Table 5.5: Remnant polarization P_r and coercive field E_c of the BCTCV sample with doping concentration.



Figure 5.20: Room temperature Polarization and rate of change of polarization Vs electric field of (A)BCTCV1, (B)BCTCV2, (C)BCTCV3, and (D) change in the Remnant polarization $2P_r$ and coercive filed $2E_c$ concerning the change in the doping concentration.

The value of 2Ec and 2Pr is been plotted as figure 5.20(D) from the data in table5.5.The value of both 2Ec and 2Pr is increasing with doping concentration.

5.5.2 Hysteresis loop for BBC

Polarization Vs electric field graph is been studied for BBC series. It is clear from the figure that all the samples are performing hysteresis loop which has proper shapes except BBC3, the hysteresis loop shows a little distorted behavior, known as double hysteresis loop [13]. we have calculated the coercive field and remnant polarization from the graph and tabulated them in table 5.6 .we have also plotted the derivative of polarization concerning the electric field to check for maxima and minima from Fig 5.21 (A) to (C). In BBC_3 we are having 4 maxima which further confirms double hysteresis loop type behavior in the sample.

Sr.	Doping	Coercive field,	Remnant polarization,
No.	concentration(%)	2E _c (kV/cm)	2P _r (nC/cm/V)
1	0	2.73	3.56
2	1.56	14.54	4.19
3	3.125	17.20	3.945

Table 5.6:Remnant polarization P_r and coercive field E_c of the BBC sample with doping concentration



Figure 5.21:Room temperature Polarization and rate of change of polarization Vs electric field of (A)BBC1, (B)BBC2, (C)BBC3, and (D) change in the Remnant polarization 2P_r and coercive filed 2E_cconcerning the change in the doping concentration.

The change is remnant polarization and the coercive field from table 5.6 is been plotted here in Fig5.21(D).It is clear from the graph that the value of Ec and Pr both increasing for BBC2 and then decreasing slightly for BBC3, which was also the case in transition temperature.

5.6 FESEM

FESEM on the sample is employed using Supra 55 Zeiss-FESEM of sintered pellets to get fine dense micro grains on the surface of the material. After that Image J software is been used to calculate the average grain size of all the samples and change in the grain size concerning the doping concentration is shown. Sintering of material results in dense matter formation with a better crystalline nature. A site to site diffusion of ions is a necessary condition to achieve such crystalline dense form during the sintering process. To materialize such an ion diffusion process, vacancies play the most useful role. Hence, the available oxygen vacancies are important factors in the grain-growth mechanism. A secondary electron image and 2-D elemental mapping of the existing material is also done to check the homogeneity of the constituent elements in the samples.

5.6.1 FESEM for BBC

Sintering of material results in dense matter formation with a better crystalline nature. A site to site diffusion of ions is a necessary condition to achieve such crystalline dense form during the sintering process. The micro-grain image of the sample from FESEM is shown here in Fig5.22 and the change in average grain size to doping concentration is also plotted in fig 5.22(D). The average grain size of the material is increased forBBC2 and then again decreases for BBC3 here. To materialize such an ion diffusion process, vacancies play the most useful role. Hence, the available oxygen vacancies are important factors in the grain-growth mechanism. A secondary electron imageFig.5.23(A) and 2-D elemental mapping of the existing material is done, and it is found that all the constituent elements were homogeneously distributed throughout the sampleFig.5.23 (B)-(F).



Figure 5.22:SEM image of (A)BBC1,(B)BBC2,(C)BBC3, and (D) Average grain growth of sample with the change in the doping concentration.



Figure 5.23:(a)Secondary electron image, elemental 2-D mapping of (b) Oxygen,(c) Titanium,(d) Barium,(e) Bismuth and (F) Copper

5.6.2 FESEM for BCTCV

The micro-grain image of the sample from FESEM is shown here in Fig5.22 and the change in average grain size concerning doping concentration is also plotted in fig 5.24(D). The average grain size of the material is increasing with doping, which was expected as both calcium and vanadium on their doping increase the average grain size.



Figure 5.24: SEM image of (A)BCTCV1,(B)BCTC2,(C)BCTCV3, and (D) Average grain growth of sample concerning a change in the doping concentration.

5.7 Conclusion and Future scope

Effect of Ca. V, Cu doping in BCTCV and Bi, Cu doping in BBC on structural, optoelectronic and ferroelectric properties has been investigated. All these samples are in crystalline structure while BCTCV1 and BCTCV2 show sign of mixed phase structure. Tetragonality of the samples is relatively increasing with doping concentration in both the series. We have confirmed vibrational modes of both the series and found they match with pure BT sample. It is observed that optical band gap of the BCTCV series is approximately constant while for BBC series it is decreasing with doping concentration. Urbach energy tail in both series is increasing with doping concentration, which means the disorder in the samples increases with doping.. The value of dielectric constant is increasing with the doping concentration in BCTCV. Value of Transition temperature first increases with small doping concentration and again decreases with further increase in doping in both series of samples. In BBC series we have observed an increase of ~20°C in the transition temperature. Modified curie Weiss law suggest that all sample in BBC series shows a ferroelectric type phase transition while in the BCTCV series the transition is becoming more relaxor type with increasing doping concentration. Both the series are performing proper PE hysteresis loop in which the value of remnant polarization and coercive electric field is increasing with the doping concentration. BBC3 is showing a double hysteresis loop. All the samples are well dense and average grain size is increasing continuously in BCTCV. In BBC series, the average grain size attains a maximum in BBC2 while in BBC1 and BBC2, the average grain size is comparable and smaller.

Future work aimed to further investigate the role of Cu^{2+} and Bi^{3+} ion doping in the parent BT ceramic .the role of cations with 3+ charges and their effect on the transition temperature and dielectric constant with co-doping can be investigated. Other than that, to investigate the role of Bi in the double hysteresis loop in the ferroelectric behavior would another focus in future research.

REFERENCES

[1] Y. Imanaka et al. (2012), The Ceramic Society of Japan, Advanced Ceramic Technologies & Products, 3 DOI: 10.1007/978-4-431-54108-0_1.

[2] Deubener, J., Journal of Non-Crystalline Solids (2018), https://doi.org/10.1016/j.jnoncrysol.2018.01.033.

[3]

https://shodhganga.inflibnet.ac.in/bitstream/10603/26634/6/06_chapt er1.pdf.

[4] Buchanan R C 1991 Electricalelectronic applications for advanced ceramics. In: Engineered Materials Handbook Ceramics and Glasses. ASM International, Materials Park, OH, Vol. 4, Sect. 15, pp. 1105±6.

[5] K. ISHIKAWA and S. MATSUYA et al.(2003)Volume 9; (ISBN: 0-08-044150-5); pp. 169.

[6] Webb, S. J., Breeze, J., Scott, R. I., Cannell, D. S., Iddles, D. M. and Alford, N. M. J. Am. Ceram. Soc., 85 (2002) 1753.

[7] Bednorz JG, Mu[.] ller KA. Phys. Rev. Lett.52 (1984) 2289.

[8] Dimitrov, V. and Sakka, S. J. Appl. Phys., 79 (1996) 1736.

[9] Binghao Wang at al. (2017) DOI:10.1021/acs.chemrev.8b00045.

[10] T.A. NirmalPeiris(2014), Microwave-assisted processing of solid materials for sustainable energy-related electronic and optoelectronic applications, Ph.D. dissertation, Monash University.

[11] DariuszBogdal (2005), Chapter 1 - Interaction of microwaves with different materials, DOI: 10.1016/S1460-1567(05)80014-5,pg.no.3-4.

[12] Arun Yadav et al. RSC Adv., 2017, 7, 39434.

[13]

[14] Y.-K.AnM.K.KimH.Sohn(2014), 4 - Piezoelectric transducers for assessing and monitoring civil infrastructures, DOI: https://doi.org/10.1533/9780857099136.86.

[15] JamesF.TresslerKenjiUchino(2000),5.22 - Piezoelectric Composite Sensors,DOI: 10.1016/B0-08-042993-9/00151-0.

[16] SidneyLang (2005), Physics Today, 58, 8, 31, DOI:10.1063/1.2062916.

[17] Ravi Anant Kishore and Shashank Priya,(2018)Materials, 11, 1433; DOI:10.3390/ma11081433.

[18] Justin Varghese(2013), Ferroelectric nanoparticles, wires, and tubes: synthesis, characterization and applications, DOI: 10.1039/c3tc00597f/

[19] Wenk, Hans-Rudolf; Bulakh, Andrei (2004). Minerals: Their Constitution and Origin. New York, NY: Cambridge University Press. ISBN 978-0-521-52958-7.

[20] Liu, Su, and Weng (2013), A phase-field study on the hysteresis behaviors and domain patterns of nanocrystalline ferroelectric polycrystals

,J. Appl. Phys. 113, 204106.

[21] Z. Cai, C. Zhu, H. Wang, P. Zhao, L. Chen, L. Li, and X. Wang, J. Mater. Chem.A (2019).

[22] J. Gao, D. Xue, W. Liu, C. Zhou, and X. Ren, Actuators 6, 24 (2017).

[23] C. Gao, Q. Fu, D. Zhou, H. Zu, T. Chen, F. Xue, Y. Hu, Z. Zheng, and W. Luo, J. Eur. Ceram. Soc. 37, 1523 (2017).

[24] P. Long, C. Chen, D. Pang, X. Liu, and Z. Yi, J. Am. Ceram. Soc. 102, 1741 (2019).

[25] Z. Yan, Y. Guo, G. Zhang, and J.-M. Liu, Adv. Mater. 23, 1351 (2011).

[26] H.Thurnaurer and J. deaderick, U.S. patent No. 2,429,588,oct.21,1947; filed (1941).

[27] M.B.Gill (2019), Effects of Mechanical Activation of Precursors in The Synthesis of Ca-Doped BaTiO3 Via Conventional Solid-State Reaction Method, Journal of Physics: Conf. Series 1191, 012053, IOP Publishing, DOI:10.1088/1742-6596/1191/1/012053.

[28] Aanchal Chawla et al.(2018), Structural, surface morphological, and ferroelectric properties of Ca doped BaTiO3 solid solutions, AIP Conference Proceedings, 020016, DOI: 10.1063/1.5052085.
[29] SAKABE et al.(2002), Dielectric Properties of Fine-Grained BaTiO3 Ceramics Doped with CaO, Jpn. J. Appl. Phys. Vol. 41 (2002) Pt. 1, No. 11B Y.

[30] M.R. Panigrahi, S. Panigrahi(2002), Synthesis and microstructure of Ca-doped BaTiO3 ceramics prepared by high-energy ball-milling, Physica B 404 (2009) 4267–4272.

[31] S-H. Yoon et al(2010): Resistance degradation behavior of Cadoped BaTiO3, J. Mater. Res., Vol. 25, No. 11.

[32] S.K. Pradhan et al.(2015), Study of Dielectric Properties of Ca Doped Barium Titanate Ceramics, AIP Conf. Proc, 1728, 020572-1– 020572-3; DOI: 10.1063/1.4946623.

[33] Sophia Sahoo et al,(2019),Enhancement of dielectric and ferroelectricproperties by Ca doping BaTiO3, AIP Conference Proceedings 2115, 030020 (2019),DOI: /10.1063/1.5112859.

[34] S. Islam et al.(2015), Synthesis and Characterization of Bismuth Doped Barium Titanate, American International Journal of Research in Science, Technology, Engineering & Mathematics, 13(1), December 2015- February 2016, pp. 28-32.

[35] N. Sareecha et al.(2017), Electrical investigations of Bi-dopedBaTiO3 ceramics as a function of temperature, Physica B: Physics ofCondensedMatter,S0921-4526(17),30964-X,DOI:10.1016/j.physb.2017.11.069.

[36] A. MAHAPATRA et al. (2014),Dielectric and Ferroelectric Behavior of Bismuth-Doped Barium Titanate Ceramic Prepared by Microwave Sintering, The Minerals, Metals & Materials Society, DOI: 10.1007/s11837-014-1266-7.

[37] X.P. Jiang et al.(2007),Dielectric and Ferroelectric Properties of Bi-doped BaTiO3 Ceramics,Key Engineering Materials Vols 334-335 (2007) pp 977-980, Trans Tech Publications, Switzerland, doi:10.4028/www.scientific.net/KEM.334-335.977.

[38] ShuangyiLiu et al. (2012)Comprehensive dielectric performance of bismuth acceptor doped BaTiO3 based nanocrystal thin film capacitors

, J. Mater. Chem., 2012, 22, 21862.

[39] Sadeghzadeh Attar A, et al. (2016) Structural and dielectric properties of Bi-doped barium strontium titanatenanopowders synthesized by sol-gel method. J Mater Res Technol. 2016,DOI: 10.1016/j.jmrt.2016.05.001.

[40] A Mishra and Niyati Mishra(2012),Influence of Copper doping on physical properties of BariumTitanate, Journal of Physics: Conference Series 365 (2012) 012009 DOI:10.1088/1742-6596/365/1/012009.

[41] MogantiVenkataSomeswara Rao et al. (2013), Effect of Copper Doping on Structural, Dielectric, and DC Electrical Resistivity Properties of BaTiO₃, Advances in Materials Physics and Chemistry, 2013, 3, 77-82.

[42] Chen Ang et al. (1999), Variable-range-hopping conduction and metal-insulator transition in Cu-doped BaTiO3, J. Phys.: Condens. Matter 11 (1999) 9703–9708.

[43] Ying-Chieh Lee et al.(2009), Effects of CuO Doping on the Microstructural and Dielectric Properties of Ba0.6Sr0.4TiO3 Ceramics, J. Am. Ceram. Soc., 92 [11] 2661–2667 (2009), DOI: 10.1111/j.1551-2916.2009.03266.x.

[44] Wei Cai et al.(2011), Vanadium doping effects on microstructure and dielectric properties of barium titanateceramics, Ceramics International 37 (2011) 3643–3650.

[45] PIOTR DULIAN et al.(2013),Dielectric properties of vanadium doped barium titanate synthesized via high-energy ball milling, International Seminar on Physics and Chemistry of Solids (ISPCS) and Advanced Materials, Cz estochowa, 12 – 15 June 2013.

[46] F. Moura et al. (2007),Ferroelectric and dielectric properties of vanadium-doped Ba(Ti0.90Zr0.10)O3 ceramics, Journal of Alloys and Compounds 466 (2008) L15–L18.

[47] E. Davis and N. Mott, Philos. Mag. 22, 0903 (1970).

[48] N. Mott and E. Davis, "Electronic Process in Non-Crystalline Materials" (Oxford, 1979), pp. 458–465. [49] Saniya Ayaz, Prashant Mishra, and SomadityaSen ," Structure correlated optoelectronic and electrochemical properties of Al/Li modified ZnO", J. Appl. Phys. 126, 024302 (2019); DOI:10.1063/1.5099894

[50] J F Scott, "Ferroelectrics go bananas", J. Phys.: Condens. Matter 20 (2008) 021001 (2pp).