STUDY THE EFFECT OF TEMPERATURE ON THE DIELECTRIC PROPERTIES OF BARIUM TITANTE FOR HIGH ENERGY CAPACITORS

By

Fatima Muqeet

Rafia Javed Zaki

Talha Saadat

School of Chemicals and Materials Engineering

National University of Sciences and Technology

2020

STUDY THE EFFECT OF TEMPERATURE ON THE DIELECTRIC PROPERTIES OF BARIUM TITANTE FOR HIGH ENERGY CAPACITORS

By

Leader: Fatima Muqeet (00000196468)

Member 1: RafiaJavedZaki (00000199393)

Member 2: TalhaSaadat (00000138145)

A THESIS

Submitted to

National University of Sciences and Technology

In partial fulfilment of the requriments for degree of

B.E. MATERIALS AND METALLURGICAL ENGINEERING

School of Chemicals and Materials Engineering (SCME)

National University of Sciences and Technology (NUST)

July, 2020

CERTIFICATE

This is to clarify that work in this thesis has been completed by Ms. Fatima Muqeet, Ms. Rafia Javed Zaki and Mr. Talha Saadat under the supervision of Dr. Mohsin Saleem and Dr. Malik Adeel Umer at the School of Chemical and Materials Engineering (SCME), National University of Science and Technology, H-12, Islamabad, Pakistan.

---------------------------------------   ----------------------------------

Advisor: Co-Advisor:

Dr.Mohsin Saleem   Dr. Malik Adeel Umer

Department of Materials Engineeering   Department of Materials Engineering

School of Chemical and Materials Engineering   School of Chemical and Materials Engineering

National University of Sciences and Technology   National University of Sciences and Technology

Submitted Through:

HOD-------------------------------------
Department of Materials Engineering
School of Chemical and Materials
Engineering
National University of Sciences and
Technology

Principal/Dean -----------------------
School of Chemical and Materials
Engineering
National University of Sciences and
Technology

DEDICATION

This thesis is dedicated to our parents, who have raised us to be a person we are today. It was a result of their untiring efforts; love and support which gave us strength to achieve this milestone. Thank you for your unconditional love, support and guidance.

ACKNOWLEDGEMENTS

ABSTRACT

Barium Titanate, $BaTiO_3$, a ferroelectric ceramic material is used as the dielectric medium in capacitors. The effect of different sintering temperatures on the ferroelectric properties was studied. $BaTiO_3$ was synthesized through a solid-state method using Barium Carbonate $BaCO_3$ and Titanium Oxide TiO_2 as precursors. The powders were mixed in ethanol as mixing medium and zirconia balls through low energy ball milling for 24 hours. After 24 hours, the mixture was dried at 75℃ and calcined at 850℃ for two hours at a heating rate of 5℃/min. The effect of different sintering temperatures was studied. The powder obtained after calcination was sintered at 1050℃, 1100℃, and 1150℃ at the heating rate of 5/min. Characterization techniques like XRD, SEM, Raman Spectroscopy, Impedance Analyzer, and Breakdown Strength were done. The formation of the tetragonal phase was confirmed through XRD and Raman Spectroscopy. The morphology and particle size were examined through SEM. Impedance Analyzer was used to find out the dielectric constant and dielectric loss values.

TABLE OF CONTENTS

LIST OF FIGURES

<div align="right">

CHAPTER 1

</div>

<div align="center">

INTRODUCTION

</div>

1.1   Background

Dielectric materials placed between the plates of a capacitor are used to store charge. Many ferroelectric materials are used as dielectric materials. They show spontaneous polarization when the external field is applied due to their crystal structure and retain that polarization even after the removal of the field. This creates a hysteresis loop which is an important characteristic of ferroelectric materials.

1.1.1   Material Selection

Barium titanate ($BaTiO_3$) is widely used ferroelectric ceramic dielectric material due to its high dielectric constant reaching 14000 and high dielectric strength with low dielectric loss. It is due to its perovskite (ABO_3) crystal structure which increases its application in the area of dielectric ceramics for capacitor application. It is used to make multilayer ceramic capacitors (MLCCs) which increases its efficiency. This depends on the grain size of the ceramic materials obtained.

Conventionally, barium titanate has been made by solid-state reaction by mixing the raw materials and then subjecting them to calcination and sintering at high temperatures. This results in obtaining the required particle size which results in the optimum requirement for the dielectric properties to be achieved.

1.1.2   Dependence of dielectric constant

The dielectric constant depends on the grain size. Achieving an optimum grain size results in higher values of dielectric constant. The optimum grain size lies in the range of 0.8-1.1 μm. Achieving grain size in this range leads to higher dielectric properties.

The dielectric constant of the dielectric medium is also dependent on the ferroelectric transition temperature of the dielectric medium which is called Curie temperature T_c. Above T_c, the material changes its ferroelectric phase to the paraelectric phase and as a result losses its ferroelectric properties. For $BaTiO_3$, this ferroelectric transition temperature is 120°C, below which it is tetragonal in the structure; the ferroelectric phase and above which it becomes cubic; paraelectric phase. It loses perovskite structure and hence its ferroelectric properties.

At T_c, a coarse grained microstructure has a higher dielectric constant than fine-grained while at room temperature, fine-grained microstructure has a high dielectric constant. Moreover, decreasing grain size can result in a lowering of Curie temperature and thus achieving a higher dielectric constant at lower temperatures than Curie temperature.

The main objective of this work is to achieve optimum grain size of $BaTiO_3$ in through solid-state reaction by mixing barium carbonate ($BaCO_3$)and titanium oxide (TiO_2) as raw materials followed by calcination and then sintering at different temperatures (1050°C, 1100°C, 1150°C) in order to optimize the variables (time and temperature) and achieve optimum properties (dielectric strength, dielectric constant).

LITERATURE REVIEW

2.1 Dielectric Materials

Dielectric materials are used in capacitors for storing charge. It is placed between the plates of the capacitor helping in the storage of charge. Many ceramic materials along with polymers have been used as dielectric materials. Ceramics act as insulators and do not allow the current to flow when an electric field is applied, hence help in storing charge. They undergo polarization that is they become charged when placed in an electric field. The charges in them slightly shift from their position forming a dipole moment. The positive ions move toward the negative plate and the negative ions move toward the positive plate of the capacitor. This helps in retaining charge before becoming conductive upon application of high voltage. This is known as dielectric strength. Many ceramic-based dielectric materials are being used in capacitors. For example, barium titanate ($BaTiO_3$), lithium niobate ($LiNbO_3$), etc. have been used as dielectric materials in capacitors. But most commonly, barium titanate is used due to high relative permittivity and high breakdown voltage. Due to their ferroelectric properties, these materials have a wide application in storing charge for capacitors.
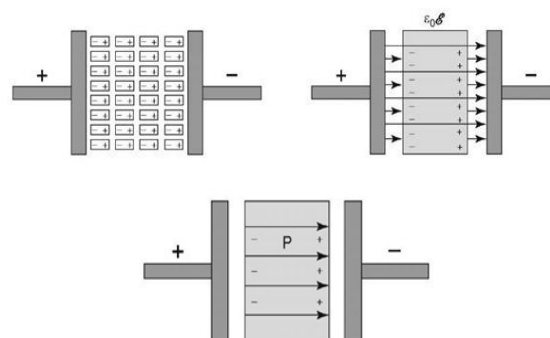
Fig 2.1 Dielectric Materials in Capacitors

2.1.1 Types of Polarization

There are various types of polarization in the material. The most common are; orientation, ionic, and electronic. These polarizations depend on the frequency of the applied voltage.

2.1.1.1 Electronic Polarization

Electronic polarization occurs in all materials at a relatively higher frequency. When the electric field is applied, the electrons orbiting around the nucleus slightly shifts towards the positive electrode while the nucleus towards the negative electrode. As a result, the atom attains a net dipole moment and the atom becomes polarized. When the electric field is removed, the temporary dipoles vanish and the electrons and nucleus come back to their original position. The charges displace through a very small distance so the overall amount of electronic polarization is less as compared to the other two.

Fig 2.2 Electronic Polarization

2.1.1.2 Ionic Polarization

Ionic polarization requires the displacement of ions within the crystal structure. The positive ions are attracted to the negative electrode while the negative ions toward the positive electrode. In the case of atoms, the atoms are being displaced upon the application of the electric field. The bonds between the atoms or ions in the crystal structure are stretched due to this mechanism.
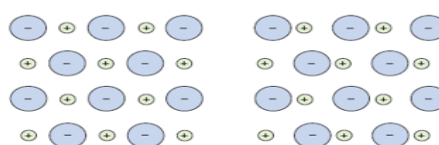
Fig 2.3 Ionic Polarization

2.1.1.3   Orientation Polarization

Orientation polarization occurs in materials that have permanent dipoles. When the electric field is applied, the permanent dipoles align themselves in the direction of the electric field. Orientation polarization is dependent on temperature. It decreases with increasing temperature due to the thermal vibration of atoms counteracting the alignment tendency.

Fig 2.4: Orientation Polarization

2.1.2   Dielectric Constant

Dielectric constant also called relative permittivity is the ratio of the permittivity of a medium to the permittivity of free space. It depends on the degree of polarization of material and also its charge storing capacity. When the material is placed in an electric field between two oppositely charged plates, it tends to polarize the material. The extent to which the material polarizes while storing charge is determined by dielectric constant. The dielectric constant or relative permittivity may be given by

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_\circ}$$

Low dielectric constant materials are used as insulators while high dielectric materials are used in capacitors for storing charge. Barium titanate has a high dielectric constant so is commonly used dielectric material for capacitors.

2.1.3   Frequency dependence of Dielectric Constant

The dielectric materials depend on the frequency of the applied field. Mostly for practical applications, the alternating current, in which voltage or field changes its direction with time, is used. So when the ac electric field is applied, the material polarizes in the direction of the applied field. But as direction is reversed, the dipoles tend to reorient with the

direction of the field. This reorientation requires some minimum amount of time to occur. The reciprocal of this minimum time is called the relaxation frequency. So when the material is subjected to an AC field, the field changes its direction so quickly that the material cannot change its dipoles continuously with the reversal of direction if the time is less than its relaxation frequency, thus not contributing to the dielectric constant. All three polarization mechanisms can be seen in a dielectric medium. Its dependence on frequency is shown. Although virtually the dielectric constant is independent on frequency, yet when a polarization mechanism ceases to function, the dielectric constant shows a rapid change.
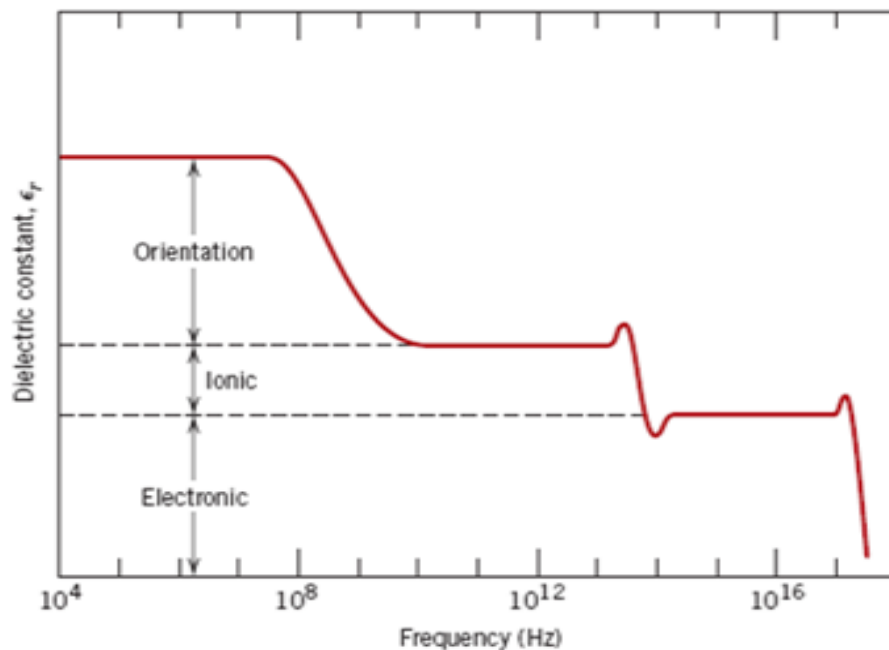
Fig 2.5: Variation of dielectric constant with frequency

2.1.4 Dielectric Loss

Dielectric materials are insulators i.e. they must not conduct electric current. Ideally, the dielectric materials must not conduct an electric current. It should only polarize when placed in an electric field. But in reality, it may absorb some amount of electric energy when placed in the ac electric field. This is termed as a dielectric loss. It may be obtained through the dissipation factor $\tan\delta$, where δ is the angle of lag between

voltage and current due to the AC field. It is defined as the measure of dielectric power loss.

2.1.5 Dielectric Strength

Dielectric materials are known for being insulators and not conducting current. But upon the use of higher voltages, even higher than the limit at which the dielectric materials can be utilized, the electrons may be excited from the valence to the conduction band. Resultantly, the current may start flowing and increase dramatically. This may cause dielectric breakdown in which localized melting, burning, or vaporization producing irreversible degradation might occur; eventually material failure. So the limit till which the dielectric material can withstand high voltage before the failure is called dielectric strength or breakdown strength. The voltage after which the dielectric material fails and starts conduction is called the breakdown voltage.

2.2. Ferroelectricity

Ferroelectricity is the spontaneous polarization of the material when the electric field is applied to it. The dipole moment is still retained even after the applied field is removed. The materials having this property are called ferroelectric materials. The ferroelectric properties of a material depend on the crystal structure of the material. The slight dipole moment in the crystal structure due to the individual ions can help to orient in the direction of the applied external field causing polarization. So even when the electric field is removed, there would be retention of polarization in the material. But these ferroelectric properties are retained in the material only till the point it changes its crystal structure. The change in the crystal structure is dependent on temperature. The temperature at which the ferroelectric material changes its crystal structure and loses its ferroelectric property is called **Curie temperature T_c.**

Dipole moments created in the ferroelectric materials form a region where they all are aligned in the same direction forming clusters. These clusters are called domains. So when the external field is applied, these

domains become aligned in the direction of the applied field showing polarization. These domains are separated by domain walls. When the applied external field is reversed, the domains also reorient themselves in their direction. But the reversal of the domains lags the reversal of filed. This creates a loop known as a hysteresis loop. All the ferroelectric materials show a hysteresis loop which follows when the electric field is applied. This is a key characteristic of the ferroelectrics.

The domains are randomly oriented in the material when the external field is zero, so overall net polarization is zero. But when the field is applied, the material becomes polarized in the direction of the applied field resulting in net polarization. The direction of polarization changes upon the reversal of the applied field. But this reversal takes time due to which ferroelectric materials obtain a hysteresis curve.
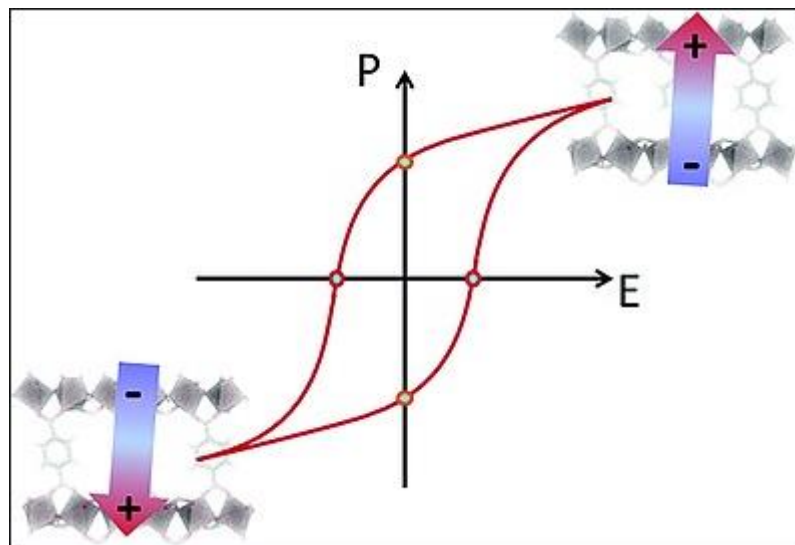
Fig 2.6 Hysteresis curve of ferroelectric materials

These ferroelectric properties vary with temperature and are retained only till the Curie temperature after which the crystal structure changes and loses the ferroelectric properties.

2.3. Ferroelectric Materials

Many ceramic materials show ferroelectric properties depending on the crystal structure. The ferroelectric materials belong to the perovskite family containing the ABO_3 type structure in which A^{+2} ions are placed on

the edges while B^{+4} ions are placed on the octahedral sites of BO_3 octahedron. These octahedrons are distorted due to the displacement of the B^{+4} ions from their octahedral position, resulting in distorted structure and not cubic at least at lower temperatures. When the temperature rises, the distorted structure changes and converts to the cubic structure at Curie temperature. So due to this distorted structure, the perovskite family have ferroelectric properties.

(a)   **(b)**
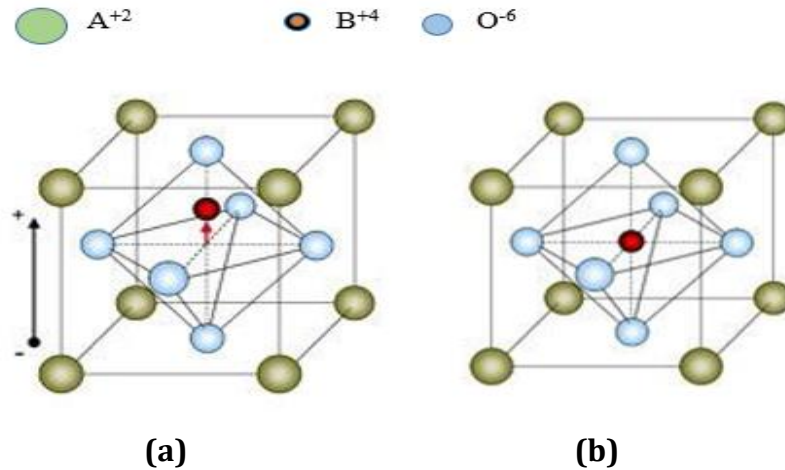
Fig 2.7Perovskite ABO_3structure (a) Distorted structure below Curie temperature (b) Cubic structure above Curie temperature

The most common examples of ferroelectric materials are; barium titanate ($BaTiO_3$), lead titanate ($PbTiO_3$), lead zirconate titanate (PZT), etc.

2.4. Barium Titanate ($BaTiO_3$)

Barium titanate is perovskite ferroelectric ceramic material which is commonly used due to its excellent ferroelectric, dielectric, and piezoelectric properties. It has ferroelectric properties due to its tetragonal crystal structure which results in a high dielectric constant as high as 14000.

Barium titanate has three polymorphs; tetragonal, cubic, and hexagonal. Out of these three polymorphs, tetragonal structure results in ferroelectric properties. It exists below the Curie temperature T_c which is 120°C. Above T_c, $BaTiO_3$ has a transition of phase from tetragonal to cubic and loses its ferroelectric properties.

The tetragonal crystal structure of $BaTiO_3$ contains barium Ba^{+2} ions placed on the edges while titanium Ti^{+4} ions are placed in the octahedral interstitial site of the octahedron. The Ba^{+2} ions are larger than their vacancies so it results in the expansion of the octahedron which causes a shift of Ti^{+4} ions toward one corner of the octahedron. Also, Ti^{+4} is too small to be stable in the octahedral interstitial site. Ti^{+4} due to its high charge shows a high degree of polarization. So upon application of field Ti^{+4} shifts from its position in the direction of the field, becoming highly polarized and resulting in high dielectric constant. The direction of shift can be altered through the application of the field. $BaTiO_3$ retains its ferroelectric properties till the T_c. After T_c, the ferroelectric phase transition occurs in which the crystal structure changes from tetragonal to cubic; Ti^{+4} ions come back to its original position at high temperature. As a result of this, $BaTiO_3$ loses its ferroelectric properties.

(a)　　　　　　**(b)**
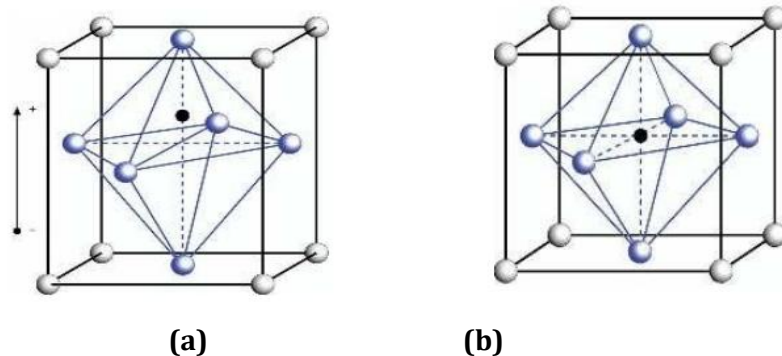
Fig 2.8 Perovskite Structure of $BaTiO_3$ (a) distorted tetragonal structure below Curie temperature (b) cubic structure above Curie temperature

The ferroelectric hysteresis of barium titanate ranging from room temperature to the Curie temperature and above may be shown as:
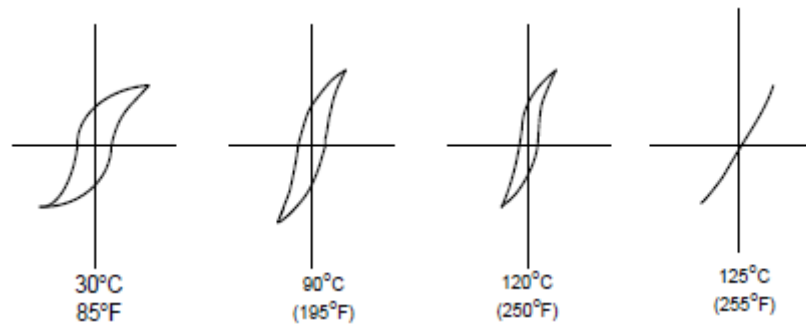
Fig 2.9 Hysteresis loop of BaTiO$_3$ with temperature

2.5. Preparation Of Barium Titanate BaTiO$_3$

2.5.1. Solid-State Reaction

Barium titanate has been prepared by many methods during the past decades. Most conventionally, the solid-state reaction has been frequently used for large scale production. The solid-state reaction involves the mixing of the initial powders in a solvent and then subjecting it to high-temperature processes (1100-1400°C).

Solid-state reactions have many advantages; being a low cost technique to easy processing. Despite the advantages of solid-state reaction technique, processing at high temperatures may result in giving large grain sizes, wide grain size distribution, and agglomeration of particles affecting the required properties.

To overcome these issues, the initial powders may be taken of smaller grain size or subject them to high energy ball milling. Also increasing the milling time may help in proper mixing and proper reduction of the particle size of the initial powders. The powder obtained after drying and calcination must be crushed properly in order to produce a fine powder.

The dielectric constant greatly depends on the grain size and crystal structure. Finer grains have a high dielectric constant at room temperature. Decreasing the grain size increases the dielectric constant. The values may reach 5000 for the product having finer nano-powders. Also, the Curie temperature that is the ferroelectric phase transition may also be decreased by decreasing grain size. This depends on the crystal structure. The grain size decreasing from micro to nano may cause a

change in crystal structure from tetragonal to pseudo-cubic. This decreases the phase transition temperature as after the Curie temperature the phase changes from tetragonal to cubic.

2.6. Application Of Ferroelectric Ceramics

Ferroelectric ceramics have been widely used recently in many technologies. The applications may include ceramic dielectric material based capacitors, sensors, actuators, ferroelectric thin films, electro-optic devices, etc. Mostly the ferroelectric ceramics like barium titanate are being used as dielectric materials for making capacitors due to high dielectric constant and breakdown strength. Hence it increases the charge storing capacity and increases the application as a dielectric medium.

EXPERIMENTAL WORK

3.1. Fabrication Of BaTiO$_3$

3.1.1   Material For Synthesis Of BaTiO$_3$

The materials used for the synthesis of BaTiO$_3$ were Barium Carbonate BaCO$_3$, Titanium Oxide TiO$_2$ powders. Both powders were of high purity in order to obtain high purity products.

3.1.2   Preparation Of BaTiO$_3$

Barium titanate was prepared by solid-state reaction of the two raw materials using low energy ball milling. The two powders were first measured to obtain a proper composition for forming BaTiO$_3$. Powders were then added in a plastic bottle. Zirconia balls of 1 and 3 mm in diameter were used in order to assure proper mixing. The balls were taken about 20% of the total mixture to be formed. Ethanol (98% pure) was used as a mixing media.

The powders were mixed in ethanol through low energy ball milling for 24 hours at 200 rpm. A solution was formed after mixing, followed by drying at 75°C in the oven for proper removal of the solvent. The sample obtained was then crushed in a gate mortar to obtain a fine powder. Calcination was carried out on the powder at 850°C for two hours in the furnace at a heating rate of 5°C/min. The calcination cycle is as follows:
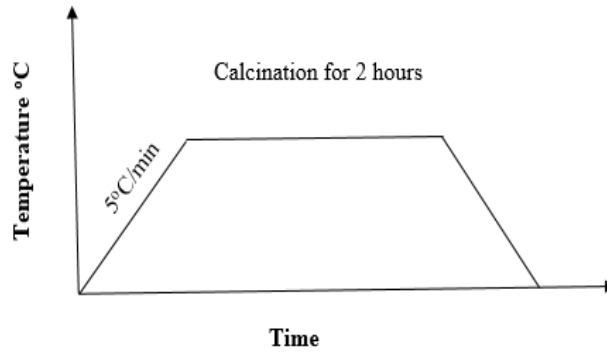
Fig 3.1 Calcination cycle

The calcined powder was then crushed and mixed with 5% Polyvinyl Alcohol (PVA) binder. Then the powder was pressed in a 13mm disc at different pressure (1, 2, 3, 5 tons) for a variable time (2, 3, 5 minutes) to optimize green density. The pellets obtained were sintered at different temperatures (1050°C, 1100°C, 1150°C). The sintering cycle was as follows; binder removal at 550°C for 30 minutes, followed by sintering involving soaking for six hours at different temperatures (1050°C, 1100°C, 1150°C), the heating rate was 5°C/min.
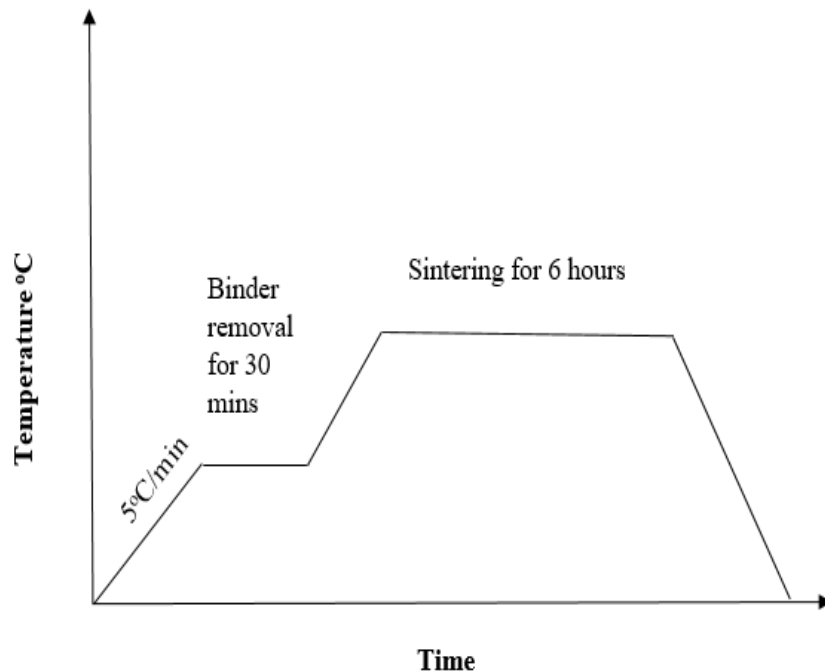
Fig 3.2 Sintering Cycle

The schematic diagram of the ball milling process for the formation of BaTiO$_3$ is as follows:

```
┌─────────────────────┐         ┌─────────────────────┐
│  Barium Carbonate   │         │   Titanium Oxide    │
│       BaCO$_3$      │         │       TiO$_2$       │
└─────────────────────┘         └─────────────────────┘
             ↓                           ↓
       ┌──────────────────────────────────────┐
       │  Mixing in ethanol for 24 hours at    │
       │  200 rpm in low energy ball milling   │
       └──────────────────────────────────────┘
                        ↓
       ┌──────────────────────────────────────┐
       │  Drying at 75$^o$C to removal         │
       │  ethaonol                             │
       └──────────────────────────────────────┘
                        ↓
       ┌──────────────────────────────────────┐
       │  Crushing                             │
       └──────────────────────────────────────┘
                        ↓
       ┌──────────────────────────────────────┐
       │  Calcination at 850$^o$C for 2 hours  │
       └──────────────────────────────────────┘
                        ↓
       ┌──────────────────────────────────────┐
       │  Pelletization and Sintering          │
       └──────────────────────────────────────┘
                        ↓
┌──────┐   ┌──────────────────────────────────────┐   ┌──────┐
│ XRD  │ ← │         Characterizations            │ → │ SEM  │
└──────┘   └──────────────────────────────────────┘   └──────┘
   ↓              ↓                    ↓
┌──────────┐  ┌──────────┐      ┌──────────────┐
│Impedance │  │Breakdown │      │   Raman      │
│Analyzing │  │ Voltage  │      │ Spectroscopy │
└──────────┘  └──────────┘      └──────────────┘
```

Fig 3.3 Flow Chart for Preparation of BaTiO$_3$

3.2 Characterization

The BaTiO$_3$ obtained after sintering was fed for different characterization techniques. Following are the characterizations carried out:

3.2.1 Phase Identification

X-ray Diffraction Technique was used to identify different phases present in the sintered product obtained. The X-Rays interact with the sample after generated from a cathode ray tube, filtered to produce a monochromatic beam of radiation, and focused on the sample. As a result of this interaction, constructive interference occurs when Bragg's Law is satisfied i.e. $n\lambda = 2d\sin\Theta$. The Bragg's Law relates the wavelength of radiation to the diffraction angle 2Θ and the lattice d-spacing of the crystalline material. The rays are diffracted from the samples which are then collected, counted, and observed. The diffraction peaks are then converted to the d-spacing, which helps in the identification of the material as each material has its own set of d-spacing. The scan angle 2Θ set was 0° to 80° to obtain the diffraction patterns of the product.

3.2.2 Scanning Electron Microscopy (SEM)

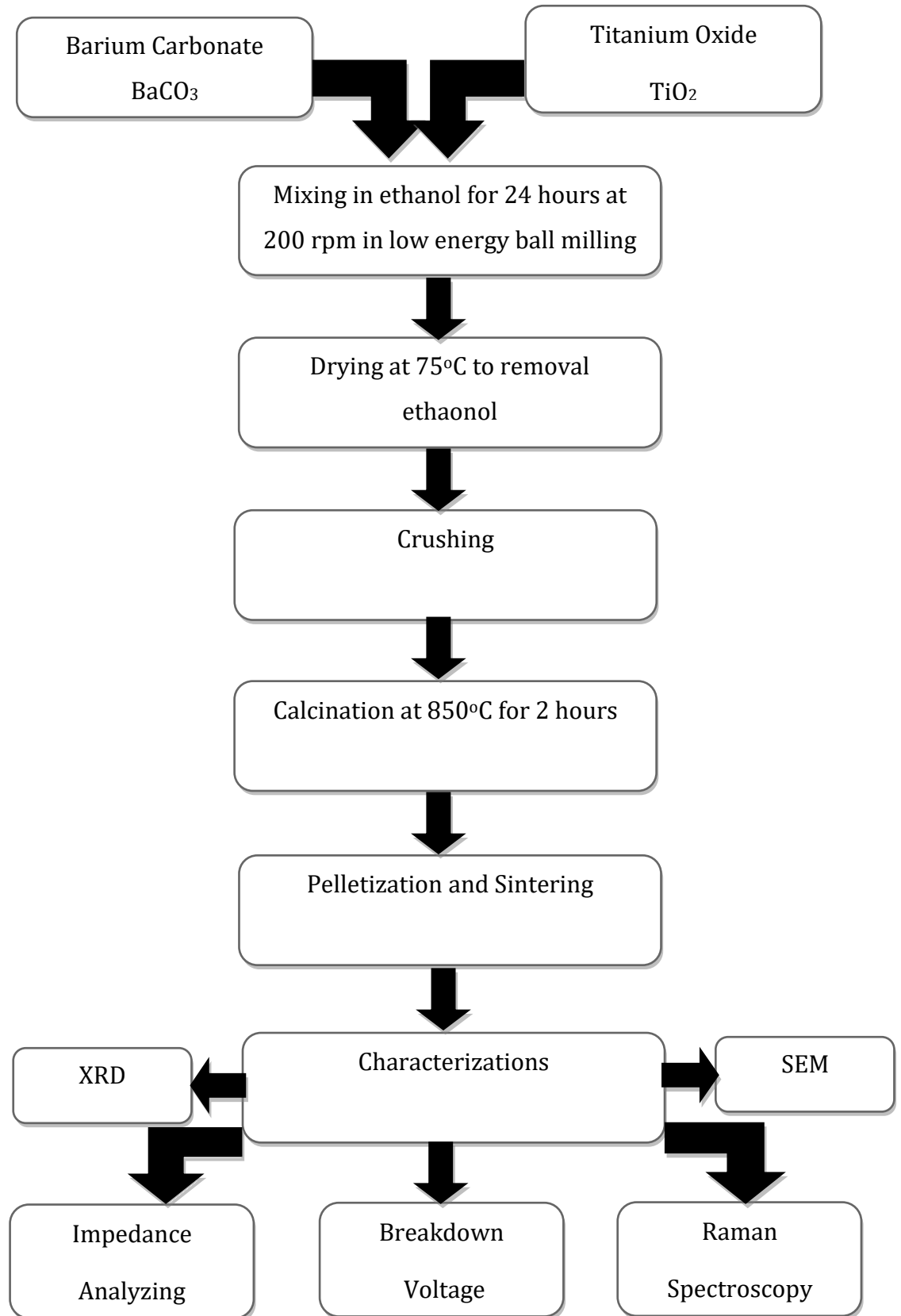Microstructural analysis was done by Scanning Electron Microscopy. In SEM, an accelerated focused beam of electrons interacts with the surface of the sample. As a result, various interactions between the surface and electrons take place which gives a variety of signals that can be used to obtain the information about surface morphology and topography. The particle morphology along with grain size, grain boundaries, and porosity were analyzed from SEM.

3.2.3 Impedance Analyzing

Dielectric constant along with dielectric loss and AC conductivity was calculated using Impedance Analyzer. Graphs between the three parameters with frequency was taken and analysis was carried out.

The **dielectric constant ε_r** of the product was calculated by the following equation:

$$\varepsilon_r = \frac{C*d}{\varepsilon_\circ *A}$$

The **dielectric loss ε''** was calculated as:

$$\varepsilon'' = tan\delta *\varepsilon_r$$

Where tanδ is the dissipation factor.

The **AC Conductivity** was measured as:

$$\sigma AC = 2\pi f * \varepsilon_\circ * \varepsilon''$$

3.2.4   Raman Spectroscopy

Raman spectroscopy was done in order to investigate the crystal structure, phase, polymorphy, and crystallinity of the material. Raman Spectroscopy is a molecular spectroscopic technique in which monochromatic light, particularly laser light is used. This light upon interaction with the molecule scatters and then this scattering is studied. The scattering is inelastic which results due to the exchange of energy between the incident photon and molecule such that the scattered photon may be of lower or higher energy than the incident photon. This energy difference obtained gives information about the rotational and vibrational energy of the molecule and also its energy levels. As a result of this, the material structure can be obtained. Raman spectra obtained were studied and analyzed.

3.2.5   Breakdown Strength

The breakdown strength of the material is found to know the maximum voltage it can withstand without failure. The breakdown strength values were obtained and analyzed.

RESULTS

4.1   Characterization of Initial Powders

4.1.1   SEM of Initial Powders

Figures below represent the initial state of $BaCO_3$ and TiO_2 prior to milling. The needle and rod-like structure of $BaCO_3$ and agglomerates of TiO_2 are obtained at a magnification of 5000x on a scale of 5µm.

(a)   (b)
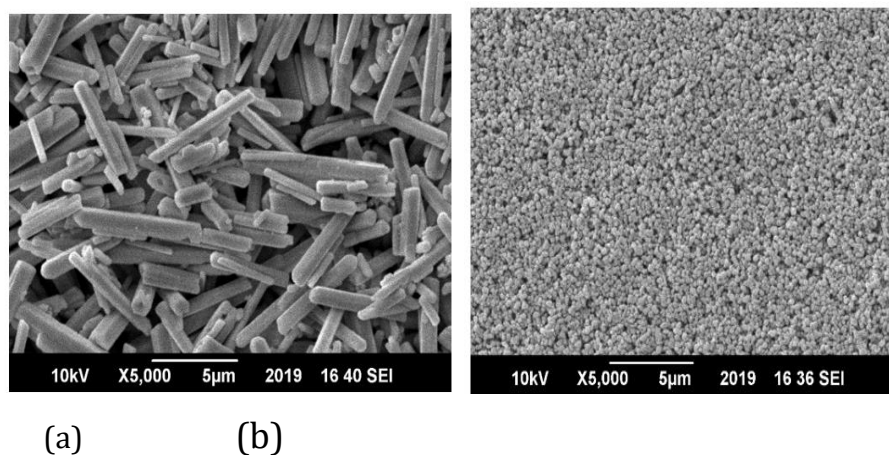
Fig 4.1 SEM of Dispersed Powder (a) $BaCO_3$ (b) TiO_2

4.2   Characterization of $BaCO_3$-TiO_2calcined powder

4.2.1   SEM of Calcined powder

Powder are calcined at 850°C for 2 hours, on heating for a certain temperature powders have enough energy to react and form segregate agglomerate particle structure. Figure 4.2 represents the rod shape of $BaCO_3$ dispersed into spheres of TiO_2 resulting in overall spherical agglomerates. The result is obtained at 5000x magnification with a particle average size of 300nm.
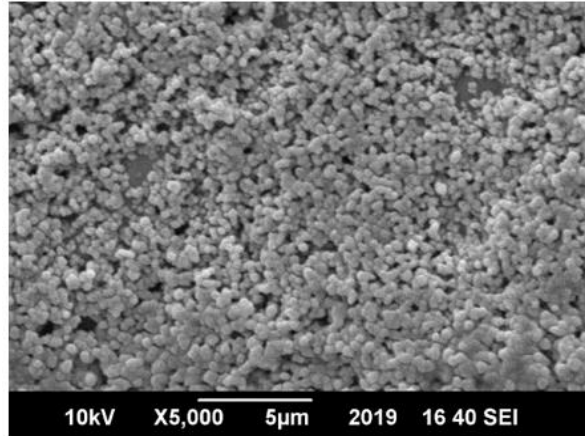
Fig 4.2 SEM of BaTiO$_3$ Powder calcined at 850°C for 2 hours

4.2.2 X-Ray Diffraction of Calcined powder

Fig 4.3 shows the XRD result of calcined powder depicting the peaks of Witherite (barium carbonate) and BaTiO$_3$. The calcination temperature of 850°C is enough for TiO$_2$ powder which reacts with BaCO$_3$ to form BaTiO$_3$ without the formation of the intermediate phase. The peaks at 2θ equal to 24.05° and 27.68° represent (021) and (002) planes of BaCO$_3$ which are then removed in sintering as seen in figure 4.5. The peaks at 2θ equal 31.7° of (101) (110) planes and 45.45° of (002) (200) planes correspond to BaTiO$_3$. This shows the formation of BaTiO$_3$ at this temperature.

Fig 4.3 X-Ray Diffraction pattern for BaCO$_3$-TiO$_2$ mixture calcined at 850°C for 2 hours

4.3 Characterization of Sintered BaTiO$_3$

4.3.1 SEM of Sintered BaTiO$_3$

Figure 4.4 below represents SEM of BaTiO$_3$ compacts, prepared by mixing PVA binder in calcined powder obtained from BaCO$_3$-TiO$_2$ mixture, sintered at different temperatures such as 1050℃, 1100℃, and 1150℃ respectively. The SEM micrographs show the effect of si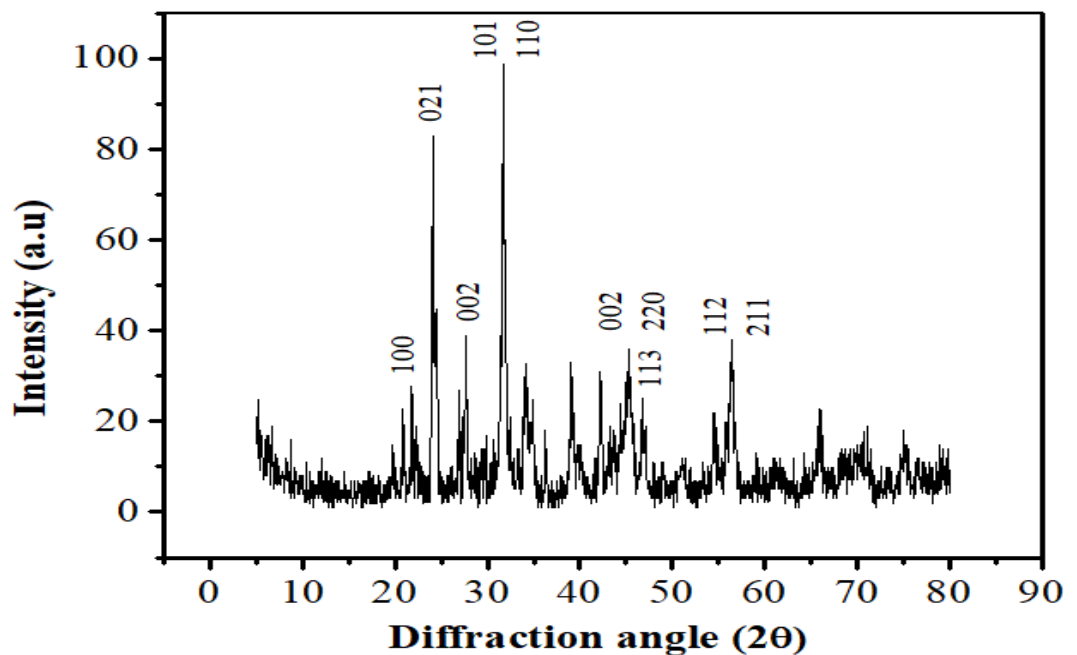ntering temperature on the grain size. It can be seen that with increasing sintering temperature, the average grain size is increased as the result of grain coursing. The average grain size at 1050℃ is found to be 0.73µm, at 1100℃ is 1.18µm and at 1150℃ is 1.89µm. While the %densification at these temperatures was 99.2%, 99.4%, and 98.7% respectively. The decrease in densification at 1150℃ is a result of overheating of the sample at this temperature which leads to a distortion of the stoichiometry of the material at high temperature. The Ba-O bond is disturbed at a higher temperature leading to any of the oxygen leaving its original position, resulting in oxygen vacancies. Hence this creates point defects which are the oxygen vacancies and increases porosity ([2] Yongquianj Tan, Jialiang Zhang, Yanqing Wu, Unfolding grain size effect in barium titanate ferroelectric ceramics). Due to this reason, the densification of BaTiO$_3$ sintered at 1150℃ results in higher porosity and lesser densification as compared to 1050℃ and 1150℃ as sintering temperature.
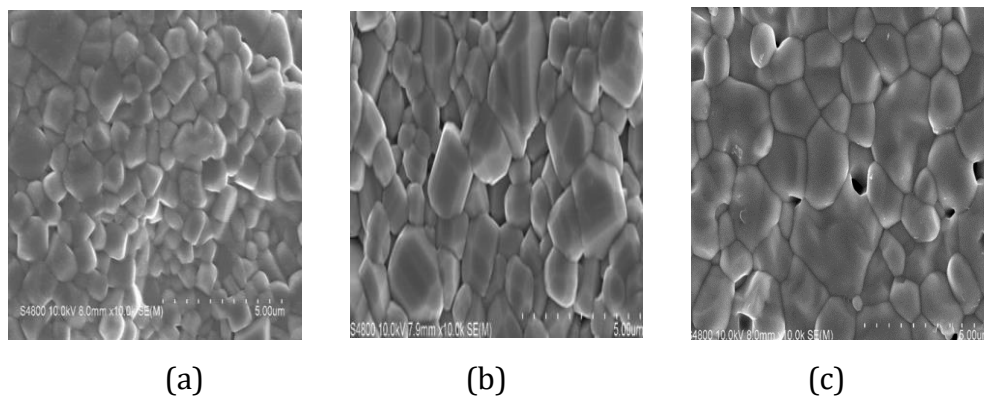

(a)   (b)   (c)

Fig 4.4 SEM of BaTiO$_3$ compacts sintered at (a) 1050℃ (b)1100℃ (c) 1150℃

4.3.2 X-Ray Diffraction of Sintered BaTiO$_3$

Fig 4.5 represents XRD patterns of sintered BaTiO$_3$at different temperatures such as 1050°C, 1100°C, and 1150°C respectively. Calcined powder is sintered at these temperatures separately at a rate of 5°C/min for 6 hours to obtain BaTiO$_3$ as the final product.

All peaks in figure 4.5 represent BaTiO$_3$ phase only, BaCO$_3$ from calcined powder mixture dissolved completely resulting in tetragonal BaTiO$_3$. The peak at 2θ equal to 22.07° shows the (001) plane of BaTiO$_3$. The specific peaks at 2θ equal to 45°explicit tetragonality of BaTiO$_3$ which can be observed via splitting of peaks- (planes (002) and (200)). The peak of (002) plane increases as compared to (200) peak upon increasing temperature which shows the increase in the tetragonality of BaTiO$_3$. The difference in the degree of tetragonality varies from temperature 1050°C to 1150°C as observed from the figure below. The overall intensity of peaks of (002) and (200) planes increases with an increase of temperature resulting in the highest form of tetragonal phase present at 1150°C sintered sample.
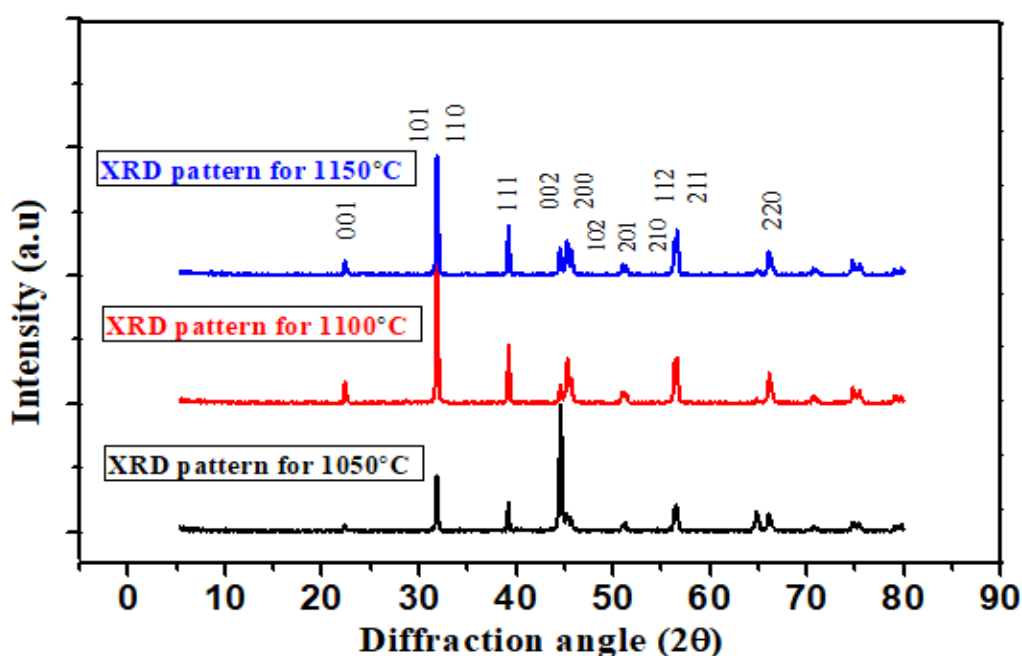

Fig 4.5 X-Ray Diffraction pattern of BaTiO$_3$ compact sintered at 1050℃, 1100℃ and 1150℃

4.3.3 Raman Spectroscopy of Sintered BaTiO$_3$

Figure 4.6 shows the Raman spectrum of BaTiO$_3$ compacts sintered at 1050°C, 1100°C, and 1150°C. The peaks obtained at different Raman shift values show the formation of the tetragonal structure of BaTiO$_3$. The peaks of 181 cm^{-1}, 246cm^{-1}, and 517 cm^{-1} show the three E (TO) bonds that are the presence of Titanium Oxygen bonds. These peaks at 181 cm^{-1}, 246 cm^{-1} and 517 cm^{-1} show the transverse optical modes of A$_1$ (TO) bond which represents the symmetry of the bonds. The modes associated to Raman shift from 150 cm^{-1} to 350 cm^{-1} are related to interaction of A site (Ba site) and to B-O (Ti-O) chains. The 302 cm^{-1} peak represents B$_1$ which shows the tetragonal structure of BaTiO$_3$. The peaks from 450 cm^{-1} to 600 cm^{-1} and around 700 represents the modes associated with vibration of oxygen atoms in BO$_6$ (TiO$_6$) octahedral. The spectrum of 1150°C is distorted due to the reason that at this temperature the stiochometry of the BaTiO$_3$ is distorted as a result of overheating.
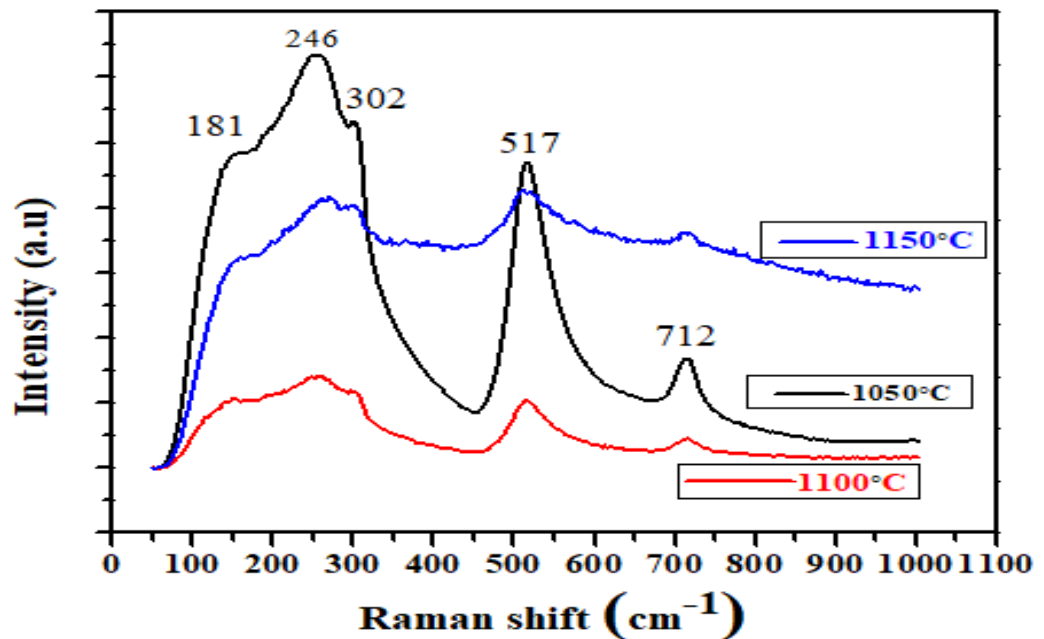

Fig 4.6 Raman Spectrum of BaTiO$_3$

4.4   Impedance Analyzing of Sintered BaTiO$_3$

4.4.1   Dielectric Constant of Sintered BaTiO$_3$

The graph below represents the dielectric constant ε_r with respect to frequency. The impedance analyzer test to find out the dielectric constant

is carried out on different sintered samples. This indeed verifies the effect of temperature on the dielectric constant of BaTiO$_3$ ceramic used as a dielectric medium at high frequencies. The dielectric constant slightly decreases with increasing frequency and then becomes stable which is an effect of the alternating current (AC) field.

The dielectric constant depends on the grain size of the material. The optimum grain size to achieve a high dielectric constant is in the range of 0.8-1.1μm. In the case of 1100℃ set as the sintering temperature, the grain size obtained was 1.18μmwith a sintered density of 99.4%. As a result of this, the BaTiO$_3$ ceramic formed at this temperature has a highest ε$_r$ value at a frequency of 5MHz around 2300 as compared to the other two (1050℃, 1150℃) sintering temperatures which have ε$_r$ values of 1750 and 1250 respectively.

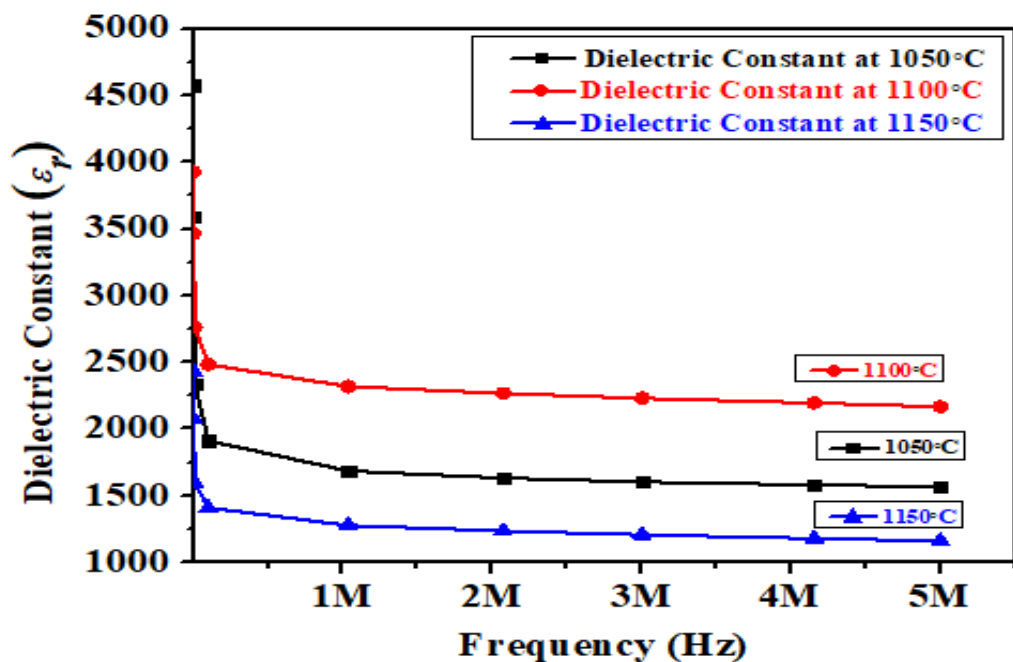
Fig 4.7 Dielectric Constant vs Frequency graph of BaTiO$_3$ ceramic for 1050℃, 1100℃ and 1150℃ sintering temperatures

4.4.2 Dielectric Loss of Sintered BaTiO$_3$

Dielectric loss is the material quantitatively dissipation of the electrical energy if the variable voltage is applied to it. As the sintered samples are of different temperatures but are composed of the same material BaTiO$_3$,

therefore the graph below represents a constant dielectric loss of $BaTiO_3$ with an increase of frequency irrespective of sintered temperatures.
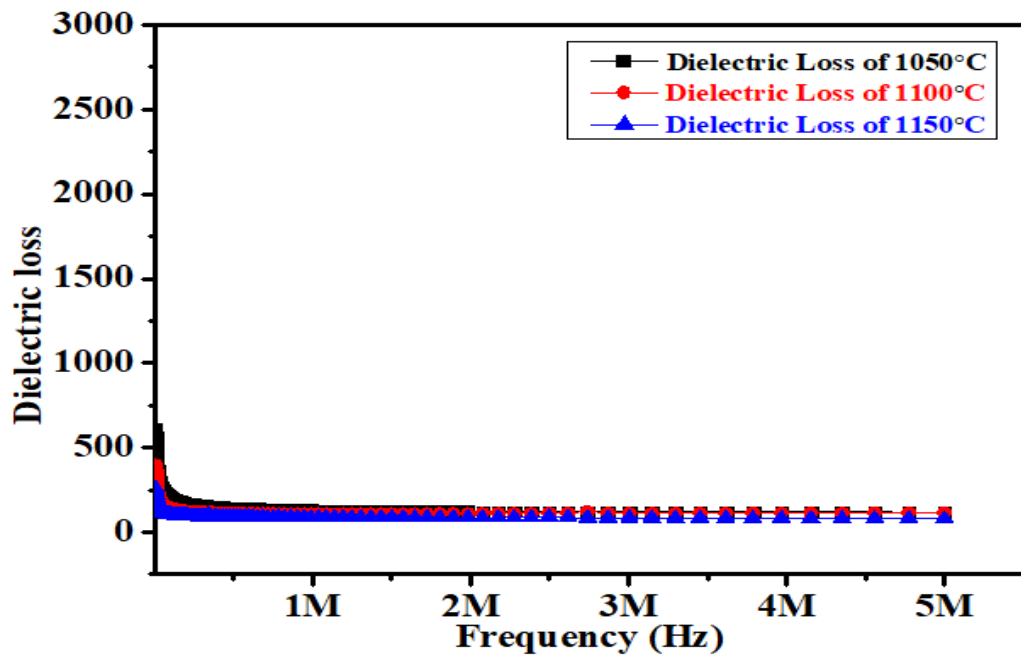
Fig 4.8 Dielectric loss vs Frequency graph of $BaTiO_3$ ceramic for 1050℃, 1100℃ and 1150℃ sintering temperature

4.4.3 AC Conductivity of Sintered $BaTiO_3$

Fig 4.9 explains the behavior of AC conductivity with respect to frequency. As frequency increases from 0 to 5MHz, the conductivity also increases. The three sintered $BaTiO_3$ samples show the same behavior, an increase in conductivity through the capability of 1050℃ and 1100℃ sintered $BaTiO_3$ to be conductive is higher than 1150℃ sintered. $BaTiO_3$ coarser grains of 1150℃ allows a maximum of 0.020 AC conductivity at a frequency of 5MHz whereas 1050℃ and 1100℃ show maximum conductivity at 0.0325. The AC conductivity depends on the dielectric loss and in turn on the dielectric constant. As 1050℃ and 1100℃ sintering temperatures have a higher dielectric constant as compared to the 1150℃ sintering temperature, so these temperatures have a higher AC conductivity.
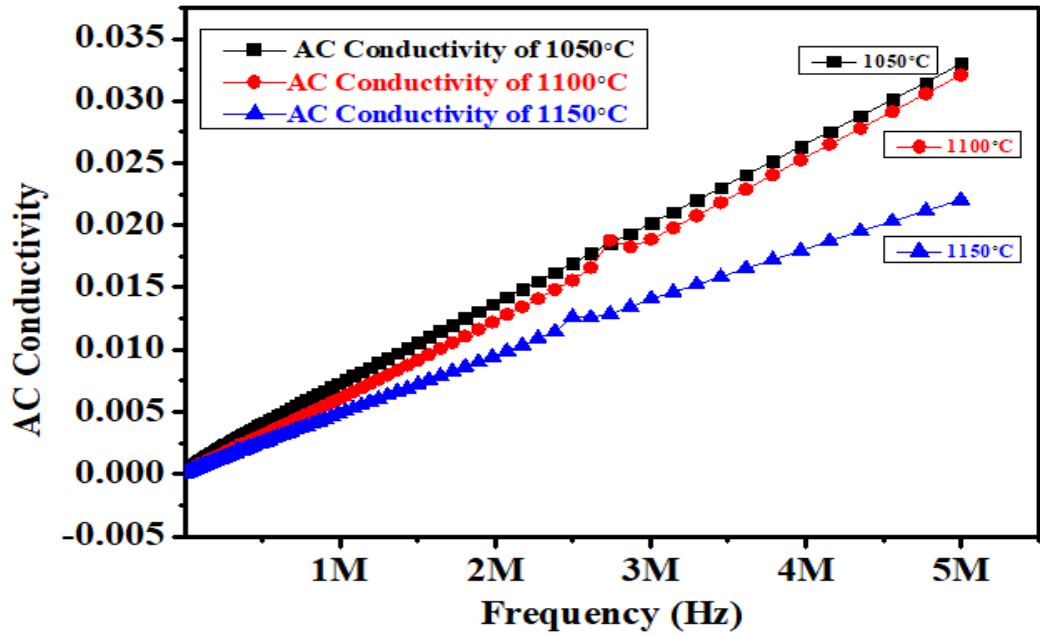
Fig 4.9 AC conductivity vs Frequency graph of BaTiO$_3$ ceramic for 1050℃, 1100℃ and 1150℃ sintering temperature

4.4.4 Dielectric Constant and Tangent Loss vs Temperature for Sintered BaTiO$_3$

Figure 4.10 represents the study of dielectric constant and tangent loss dielectric loss with respect to temperature change. The curves in the graph represent the change in dielectric constant ε_r with an increase of temperature and the tangent loss with temperature.

For 1100℃ sintered BaTiO$_3$dielectric constant gradually increases up to 90℃, a sharp increase is observed in dielectric constant up to 8000 at a temperature range of 90-95℃. Further, a steep decline in dielectric constant with an increase in temperature is observed. The same trend is also seen for 1150℃ sintered BaTiO$_3$. The peak is obtained at a temperature range of 95-100℃ and at 9000.

Fig 4.10 Dielectric Constant and Tangent loss vs Temperature graph of BaTiO$_3$ ceramic for 1100℃ and 1150℃ sintering temperature

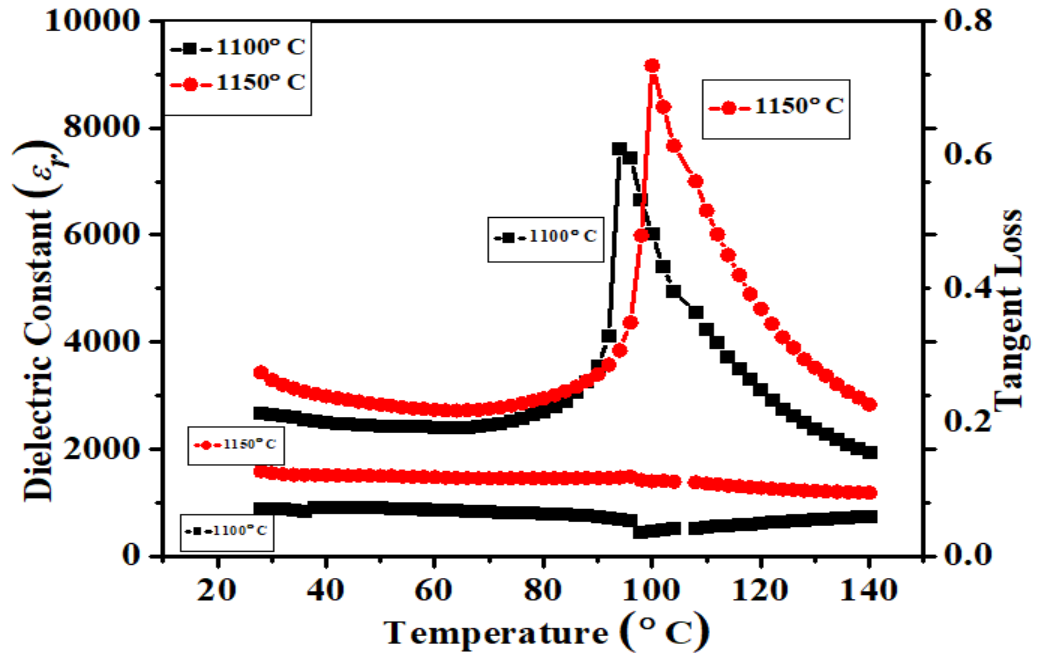The reason for the sharp increase within that temperature range lies in the Curie temperature T_c of the BaTiO$_3$. Curie temperature T_c is the temperature at which material changes its ferroelectric phase, which also depends on the grain size of the ferroelectric medium. The value of ε_r is maximum at the T_c because at this temperature, all the domains are aligned within the grain. The ferroelectric phase transition temperature of BaTiO$_3$ is 120℃.

In fig 4.10, the sharp increase in both the 1100℃ and 1150℃ is obtained around 95-100℃. The reason for this is the grain size. As grain size decreases, fine grains are formed which decreases the T_c. The more is the number of grains per square inch the lesser is the T_c. This effect is more prominent in coarser ceramics. But also at T_c, the sample having coarser grains have higher ε_r as compared to fine grains due to the formation of multiple domains in a single grain. Fine grains form small or single domains in each grain at T_c due to which the domain wall movement is restricted, the domains align with difficulty, and as results ε_r decreases. However, at room temperature, fine-grained samples have a higher ε_r as compared to coarse grains.

Tangent loss or dissipation factor $\tan\delta$ is dependent on dielectric loss which in turn depends on the dielectric constant ε_r. It is the ratio of dielectric loss to dielectric constant. The material which exhibits higher dielectric constant will have a lower tangent loss. As seen in fig 4.8, at higher frequencies, the dielectric loss is constant for both 1100℃ and 1150℃ while dielectric constant for 1100℃ is higher as compared to 1150℃. So as shown in Fig 4.10, 1100°C sintered BaTiO$_3$ having a higher dielectric constant also shows lower tangent loss compare to 1150℃ sintered BaTiO$_3$. Tangent loss graph shows a constant straight line with an increase of temperature in both sintered BaTiO$_3$ samples because it is more dependent on the dielectric constant than on the Curie Temperature T_c.

4.4.5 Breakdown Strength of Sintered BaTiO$_3$

Breakdown strength or breakdown voltage is the maximum voltage a dielectric medium can withstand before conducting electricity. It is dependent on the charge storing capacity of the material which is capacitance. The breakdown strength of BaTiO$_3$ for each sintering temperature is calculated. Figure 4.11 shows the breakdown strength vs the sintering temperature graph which shows that 1100℃ has the highest breakdown strength as compared to 1050℃ and 1150℃. At this temperature, the highest dielectric constant is achieved which shows that it is capable to store more charge due to the maximum capacitance as compared to the other sintering temperatures. As a result of this, BaTiO$_3$ ceramic formed by sintering at 1100℃ has the highest breakdown strength, which means it has the capability to withstand high voltages. Also at these specific temperature polarization enhances causing electric field which stores enough charge. Once the temperature exceeds within the range, capacitance decreases as it exceeds the breakdown strength of the dielectric medium.
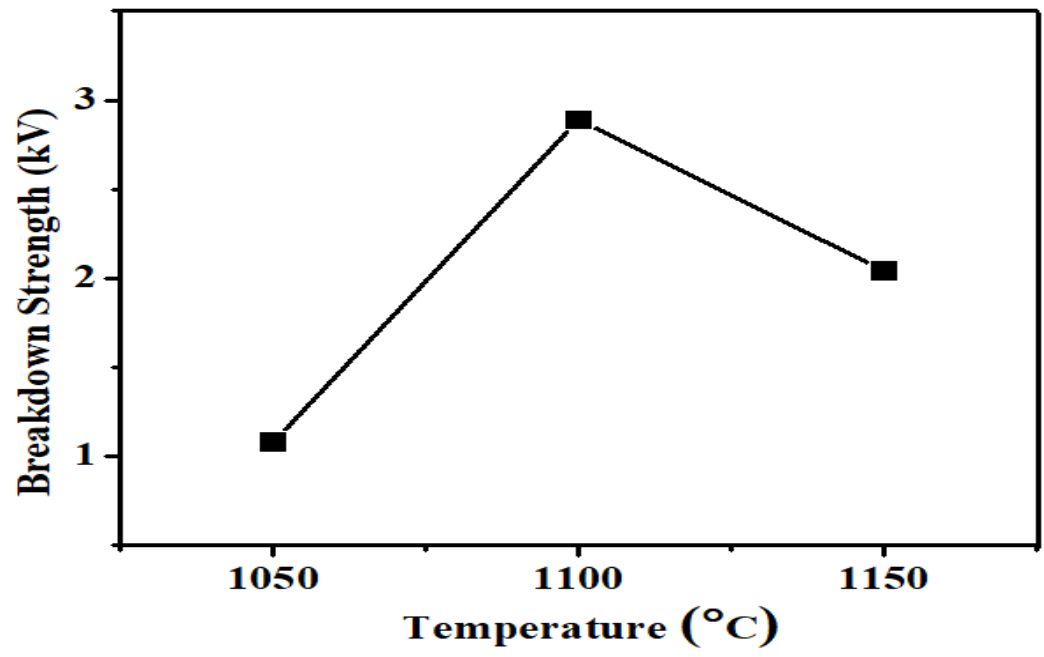
Fig 4.11 Breakdown Strength vs Sintering Temperature graph of

BaTiO$_3$ ceramic

CONCLUSIONS

In this project, Barium Titanate BaTiO₃ was synthesized by solid-state reaction using Barium Carbonate BaCO₃ and Titanium Oxide TiO₂ as precursors. The conclusions from the study can be summarized as:

1. Milling time of 24 hours in low energy ball milling, followed by drying at 75°C, calcination at 850°C for 2 hours at the rate of 5°C/min, mixing of PVA binder and then sintering at 1050°C, 1100°C and 1150°C for 6 hours at the rate of 5/min, resulted in the formation of a single-phase tetragonal BaTiO₃ with perovskite structure.

2. The XRD patterns confirmed the formation of BaTiO₃ tetragonal phase by the splitting of (002) and (200) peaks at 2θ equal to 45° which increases with increasing sintering temperature. The tetragonality of BaTiO₃ increases with increasing sintering temperature.

3. The Raman Spectrum also confirms the formation of tetragonal BaTiO₃ by showing the 303^{-1} peak of Raman Shift.

4. The dielectric constant ε_r value obtained is the highest at 1100°C, approximately 2300 at a frequency of 5MHz with minimum tangent loss. This is due to the achievement of an optimum grain size of around 1.18μm and maximum densification of 99.4% at this temperature as compared to the other two sintering temperatures.

5. Curie temperature is achieved to be 95°C for 1100°C sintered BaTiO₃ and 100°C for 1150°C sintered BaTiO₃ which is due to the formation of a relatively fine-grained structure at these temperatures. The dielectric constant for 1150°C at a Curie temperature of 100°C if found to be 9000.

6. The breakdown strength obtained was highest for 1100°C as compared to the other two sintering temperatures which are due to the fact that it has the highest densification and least porosity. This

resulted in its capability to withstand high voltages as compared to the BaTiO$_3$ ceramic obtained at 1050°C and 1150°C.

7. High energy capacitors can be formed from BaTiO$_3$ having good stability at high temperatures.

REFERENCES

[1].   Kolthoum Ismail Osman, Synthesis and Characterization of BaTiO$_3$ Ferroelectric Material, 2011.

https://inis.iaea.org/collection/NCLCollectionStore/_Public/44/079/440 79115.pdf

[2].   Yongquianj Tan, Jialiang Zhang, Yanqing Wu, Unfolding grain size effect in barium titanate ferroelectric ceramics, Scientific Reports 5 Article Number 9953, 2015.

https://www.nature.com/articles/srep09953

[3].   Z. Lazarevic, N. Romcevic, M. Vijatovic, Characterization of Barium Titanate Ceramic Powders by Raman Spectroscopy, 2008

http://przyrbwn.icm.edu.pl/APP/PDF/115/a115z412.pdf

[4].   Yongquianj Tan, Jialiang Zhang, Yanqing Wu, Unfolding grain size effect in barium titanate ferroelectric ceramics, Scientific Reports 5 Article Number 9953, 2015, Table 1, Dielectric and piezoelectric properties of the poled BaTiO$_3$ ceramics prepared from micro-sized and nano-sized powders at room temperature.

https://www.nature.com/articles/srep09953/tables/1

[5].   C.J. Xiao, C.Q. Jin, X.H. Wang, The fabrication of nano-crystalline BaTiO$_3$ ceramics under high temperature and high pressure, Journal of Materials Processing Technology, Volume 209, Issue 4, pg 2033-2037, 2009.

https://www.sciencedirect.com/science/article/pii/S092401360800394 4

[6].   Mohsin Saleem, InSoon Kim, J.S. Song, Synthesis, Sintering and Dielectric Properties of a BaTiO$_3$- Ni composite, 2014.

https://www.researchgate.net/publication/262423966_Synthesis_sinteri ng_and_dielectric_properties_of_a_BaTiO3-Ni_composite

[7].   Detlev F.K. Henning, B. Seriyati Schreinemacher, Herbert Schreinemacher, Solid-state preparation of BaTiO$_3$ – based dielectric, using ultrafine raw materials, 2004.

https://ceramics.onlinelibrary.wiley.com/doi/abs/10.1111/j.1151-2916.2001.tb01094.x

[8]. Madona Boulos, Sophie Guillemet-Fritsch, Fraçois Mathieu, Hydrothermal synthesis of nano-sized $BaTiO_3$ powders and dielectric properties of corresponding ceramics, Solid State Ionics, Volume 176, Issues 13-14, pg 1301-1309, 2005.

https://www.sciencedirect.com/science/article/pii/S0167273805000573

[9]. Lei Zhang, Jiaxin Wen, Zixi Zhang, Enhanced dielectric properties of $BaTiO_3$ based on ultrafine powders by two step calcination, Physica B: Condensed Matter, Volume 560, pg 155-161, 2019.

https://www.sciencedirect.com/science/article/pii/S0921452619300559

[10]. Maria Teresa Buscaglia, Marta Bassoli, Vincenzo Buscaglia, Solid-state synthesis of ultrafine $BaTiO_3$ powders from Nano-crystalline $BaCO_3$ and TiO_2, 2005.

https://ceramics.onlinelibrary.wiley.com/doi/full/10.1111/j.1551-2916.2005.00451.x

[11]. Kolthoum I.Othman, Ahmed A. Hassan, Umer Abdelal Ahmad Abdeal, Formation-Mechanism-of-Barium-Titianate-by-Solid-State-Reactions, 2014.

https://www.researchgate.net/publication/267927092_Formation-Mechanism-of-Barium-Titanate-by-Solid-State_Reactions

[12]. A. Kaya, S. AliAly, S. Demirezen, The investigation of dielectric properties and ac conductivity of Au/GO-doped PrBaCoO nano-ceramic/n-Si capacitor using impedance spectroscopy method, Ceramics International, Volume 42, Issue 2, Part B, pg 3322-3329, 2016.

https://www.sciencedirect.com/science/article/pii/S0272884215020325

[13]. Nurazila Mat Zali, Che Seman Mahmood, Siti Mariam Mohamad, X-ray diffraction study of crystalline barium titanate ceramics, 2015.

https://aip.scitation.org/doi/pdf/10.1063/1.4866124

[14].   M.Karimi-Jafari, K. Kowal, E. Ul- Haq, Spark Plasma Sintering of Lead-Free Ferroelectric Ceramic Layers, Topic 3.22 Reference Module in Materials Science and Materials Engineering, Volume 3, Pages 347-357, 2017.

https://www.sciencedirect.com/science/article/pii/B978012803581809 2031

[15].   Zhe Zhao, Vincenzo Buscaglia, M. Viviani, Grain- Size Effect on the Ferroelectric Behavior of Dense Nanocrystalline BaTiO, 2004.

https://www.researchgate.net/publication/230758322_Grain-Size_Effects_on_the_Ferroelectric_Behavior_of_Dense_Nanocrystalline_Ba TiO

[16].   X. Zhao, W. Liu, W. Chen. S. Li, Preparation and properties of $BaTiO_3$ ceramics from the fine ceramic powder, Ceram Intl, 41(1), S111-S116 2015.

[17].   H. Kim et al, Fabrication of bulk piezoelectric and dielectric $BaTiO_3$ ceramics using paste extrusion 3D printing technique, J. American. Ceram. Soc 102(6), 3685, 2018.

[18].   Professor J. Javier, An Introduction to Raman Spectroscopy, 2014. https://analyticalscience.wiley.com/do/10.1002/sepspec.1882education /full/

[19].   Vignaswaran K. Veerapandiyan, Saman Khosravi H, Giovanna-Canu, B-site vacancy induced Raman scattering in $BaTiO_3$-based ferroelectric ceramics, Journal of the European Ceramic Society, Volume 40, Issue 13, pg 4684-4688, 2020.

https://www.sciencedirect.com/science/article/pii/S095522192030402 7

[20].   Anastasia Kholodkova, Marina. Nikolevna. Danchevskaya, Yurii Ivakin, Crystalline barium titanate synthesized in sub- and supercritical water, 2016.

https://www.researchgate.net/publication/304746093_Crystalline_bariu m_titanate_synthesized_in_sub-_and_supercritical_water

[21]. Vincenzo Buscaglia, Clive A. Randall, Size and scaling effects in barium titanate. An overview, Journal of the European Ceramic Society, Volume 40, Issue 11, pg 3744-3748, 2020.

https://www.sciencedirect.com/science/article/abs/pii/S0955221920300315

[22]. Hirocmichi Hayashi, Takashi Nakamura, Takeo Ebina, In-situ Raman Spectroscopy of $BaTiO_3$ particles for tetragonal-cubic transformation, Journal of Physics and Chemistry of Solids, Volume 74, Issue 7, pg 957-962, 2013.

https://www.sciencedirect.com/science/article/abs/pii/S0022369713000668