SYNTHESIS AND CHARACTERIZATION OF BARIUM TITANATE-CNT COMPOSITE BY SOL-GEL TECHNIQUE

A thesis

submitted in partial fulfillment of the requirement for the award of the degree of Master of Technology in Material Engineering Department of Metallurgical and Material Engineering Faculty of Engineering and Technology Jadavpur University Kolkata-700032

By

Aritra Majumder

Exam Roll No - M4MAT19022 Class Roll No- 001711303021 Registration no - 140911 of 2017-2018

Under the supervision of

Prof. Pravash Chandra Chakraborti

Department of Metallurgical and Material engineering Jadavpur University Kolkata-700032

Dr. Barun Kumar Sanfui

Assistant Professor of Ceramic Technology Department of Ceramic Technology Govt College of Engg. & Ceramic Technology Kolkata-700010

May 2019

JADAVPUR UNIVERSITY FACULTY OF ENGINEERING AND TECHNOLOGY

CERTIFICATE

This is to certify that the thesis entitled **"SYNTHESIS AND CHARACTERIZATION OF BARIUM TITANATE-CNT COMPOSITE BY SOL-GEL TECHNIQUE"** submitted by Aritra Majumder (Exam Roll No - M4MAT19022, Class Roll No- 001711303021, Registration no - 140911 of 2017-2018) in partial fulfilment for the degree of Master of Technology in Material Engineering from the Metallurgical and Material Engineering Department, Jadavpur University, Kolkata-700032, is an authentic work carried out by him under our supervision and guidance. To the best of my knowledge, the matter embodied in this thesis has not been submitted to any other organization.

Prof. Pravash Chandra Chakraborti Thesis Advisor Dept. of Metallurgical and Material Engineering Jadavpur University Kolkata-700032

Dr. Barun Kumar Sanfui Thesis Advisor Dept. of Ceramic Technology Government College of Engineering & Ceramic Technology Kolkata-700010

Prof. Akshay Kumar Pramanick Head of Department Dept. of Metallurgical and Material Engineering Jadavpur University Kolkata-700032

Dean FET, Jadavpur University Kolkata-700032

DECLARATION OF ORIGINALITY AND COMPLIANCE OF ACADEMIC ETHICS

I do hereby declare the thesis contents literature review and original research work by the undersigned candidate, as part of my Master of Technology in Material Engineering, studies during academic session 2018-2019.

All information in this document has been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that I have fully cited and referred all the material and results that are not original to this work.

Name- Aritra Majumder Exam Roll no- M4MAT19022 Class Roll no- 001711303021 Registration no-140911 of 2017 - 2018

Signature-----Date-----

JADAVPUR UNIVERSITY FACULTY OF ENGINEERING AND TECHNOLOGY

CERTIFICATE OF APPROVAL

The foregoing thesis is hereby approved as a credible study of an engineering subject carried out and presented in a manner satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse any statement made, opinion expressed or conclusion drawn there in but approved the thesis only for the purpose for which it has been submitted.

Signature of the Final Examiners for Evaluation of Thesis along with the date.

• _____

• -----

• _____

ACKNOWLEDGMENT

I would first like to thank my thesis advisor Prof. Pravash Chandra Chakraborti, Department of Metallurgical and Material Engineering, Jadavpur University and Dr. Barun Kumar Sanfui, Assistant Professor of Ceramic Technology, Department of Ceramic Technology, GCECT for their continuous support during my research work. Their patience, motivation, enthusiasm, and immense knowledge and valuable guidance helped me all the time during my research and writing of this thesis. Without their passionate participation and input, the validation survey could not have been successfully conducted.

I would also take this opportunity to express my gratitude to all the faculty members and especially the head of the department Prof. Akshay Kumar Pramanick and Prof. Krishnendu Chakraborty, Principal of GCECT for their immense help and cooperation during the coursework of this thesis.

I am also thankful to all my friends who helped me during this post-graduate course. I would like to convey my deepest regards to Mr. Savan Kumar Sharma, Miss Paromita Das and Miss Satavisha Chatterjee for their continuous support and valuable inputs, without which this work would not have been completed. Their constant assistance and support always encouraged me to perform well. Most importantly, I must express my very profound gratitude to my parents and my family for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them.

Thank you.

(Aritra Majumder) M.Tech in Material Engineering Metallurgical and Material Engineering Department, Jadavpur University Kolkata-700032

SL No.	Торіс	Page No.
	Chapter 1	
1	Introduction	2
	Chapter 2	
2	Literature Review	6
2.1	Dielectric Materials	7
2.1.1	Dielectric Constant	7
2.1.2	Dielectric Loss	8
2.2	Nanomaterials	8
2.3	Composites	8
2.4	Electrical Ceramic	8
2.4.1	Polarization in Electrical Ceramics	9
2.4.1.1	Electronic Polarization	10
2.4.1.2	Orientation Polarization	10
2.4.1.3	Atomic Polarization	11
2.4.1.4	Space Charge Polarization	11
2.4.2	Piezoelectricity	11
2.4.3	Pyroelectricity	12
2.4.4	Ferroelectricity	12
2.5	Perovskites	13
2.6	Barium Titanate	14
2.6.1	Synthesis of Barium Titanate	16
2.6.1.1	Solid State Reaction Method	16
2.6.1.2	Hydrothermal Synthesis	17
2.6.1.3	Coprecipitation Method	17
2.6.1.4	Mechanochemical Method	18
2.6.1.5	Sol-Gel Method	18
2.7	Carbon Nanotubes	19
2.7.1	Structure and Property of Carbon Nanotubes	20
2.7.2	Electrical conductivity of Carbon Nanotubes	21
2.8	Advancement and review of previous work	22
	Chapter 3	
3	Objective	28
	Chapter 4	
4	Experimental	30
4.1	Starting Material	30

INDEX

4.2	Procedure	30
4.2.1	Preparation of pure Barium Titanate Sol	30
4.2.2	Preparation of CNT dispersed BaTiO3 Sol	31
4.3	Calcination	32
4.4	Some experimental photographs	33
4.5	Sample Characterization	35
4.5.1	Fourier Transform Infrared Spectroscopy study	35
4.5.2	Differential Thermal Analysis study	35
4.5.3	Xray-Diffraction Study	35
4.5.4	Scanning Electron Microscopy	36
4.5.5	Raman Spectrometry Study	37
4.5.6	UV-Vis Spectrometry Study	37
	Chapter 5	
5	Results and Discussion	39
5.1	Fourier Transform Infrared Spectroscopy Analysis	39
5.2	Differential Thermal Analysis	43
5.3	Phase Analysis by Xray diffraction	45
5.4	Surface Morphology study	49
5.5	Raman Spectroscopic study	50
5.6	UV-Vis Spectroscopy Analysis	52
	Chapter 6	
6	Conclusion	56
	Scope for further research	57
	References	58

Chapter 1 INTRODUCTION

1. Introduction

Barium titanate is an important ferroelectric crystal whose outstanding electrical and optical properties make it an important material for numerous applications. Barium titanate is used as a dielectric material for ceramic capacitors, and as a piezoelectric material for microphones and other transducers. Barium Titanate has been discovered during World War II circa 1941 in the United States and is being studied approximately for the past 80 years. At least in the U.S.A, the research was accelerated because of the war, researches were aggressively searching for a substitute of Mica, which was used in capacitors. Ferroelectric ceramics are the group of dielectrics having the property of spontaneous polarization (i.e., they retain a dipole moment even after the applied external electric field has been removed). The key characteristics of a ferroelectric crystal are that the direction of the polarization can be reversed by application of an electric field, and they show a type of nonlinearity known as Hysteresis. Ferroelectrics have two major characteristics, (i)asymmetry and (ii)high dielectric constant. D. W. Richerson et al & N. Nikulin et al[7,8] They reviewed the synthesis criteria as a function of the starting material and of the form of the final product (powder, film, monolith, and fiber). The ferroelectric BaTiO3 thin film is used in electronic [11-14] and electro-optic devices [15-17] due to its high permittivity phenomena, associated with the basic ferroelectric behavior. Barium Titanate in its purest form it is an electrical insulator. However, on doping with small amounts of metals, especially Scandium, Yttrium, Neodymium, etc. it becomes semiconducting. In the polycrystalline form, Barium Titanate shows a positive temperature coefficient of resistivity (PTCR).

The first detailed description of the crystal structure of BaTiO3 in the high was proposed by Helen D. Megaw (1945) in the United Kingdom and confirmed soon after with the work of Miyake and Ueda (1946). Figure 1.1 shows the perovskite structure of Barium Titanate.



Figure 1.1 Structure of Barium Titanate

Figure 1.1 shows the basic perovskite structure of $BaTiO_3$ with the Barium ion in the center of the cell and Titanium ions inside the oxygen octahedra. Barium titanate appears white as a powder and is transparent when prepared as large crystals. It is an inorganic ceramic material, which exists in one of five polymorphs depending on temperature.

The molar mass of pure Barium Titanate is 233.192 g. Its is odorless white crystalline powder with the melting point being 1,625 °C (2,957 °F; 1,898 K). Insoluble in water, however slightly soluble in dilute mineral acids; dissolves in concentrated hydrofluoric acid. In its bulk form at RT(room temperature), the optical bandgap is 3.2 eV, but this bandgap increases to ~3.5 eV when the particle size is reduced from about 15 to 7 nm [21]. Above 120°C, barium titanate has a cubic structure. This cubic phase shows no ferroelectric property, this means it possesses no spontaneous dipole and centrosymmetric, centrosymmetric crystals show no piezoelectric phenomenon due to loss of spontaneous dipole moment. With less or no dipoles the material behaves like a simple linear dielectric, giving a linear polarisation. Curie Temperature(T_c) for barium titanate is $120^{\circ}C[22]$.

Many authors have used the sol-gel technique for the synthesis of oxide-based materials like Barium Titanate [2-6]. The structural and physical properties of the gel are strongly dependent on (i)selection of starting material, (ii) rate of hydrolysis (iii) condensation, (iv) chemical modifications of the sol-gel system and (v)other processing parameters [3]. We selected Barium acetate and Ti(IV) isopropoxide for Barium and Titanium precursor. The sol-gel method by far is the most convenient method for the preparation of both thin films and powder ceramic material[1]. The sol-gel method has been chosen for the preparation of Barium Titanate due to the advantages associated with.



Figure1.2 Sol-Gel process

This method has prospective control over the morphological and surface properties of the materials. The sol-gel method in few steps delivers the final metal oxide. Those steps are hydrolysis, condensation, and drying process. The formation of metal oxide involves various adjacent steps, initially, the chosen metal precursor undergoes rapid hydrolysis to produce the metal hydroxide solution, hydrolysis is followed by immediate condensation which leads to the formation of three-dimensional gels(a semi-solid networked mass). Then, the obtained gel is subjected to the drying process, and the resulting product is readily converted to Xerogel or Aerogel-based on the mode of drying. The steps for the production of metal oxide via the solgel route is shown in Figure 1.2. In the solgel process, chemical nature of metal precursor and the solvent medium plays a vital role in the synthesis of metal oxides particles[19].



Figure 1.3 Solgel Flowchart

Carbon nanotubes were discovered in 1991 by Dr. Ijima of Japan. While buckyballs are round, carbon nanotubes are cylinders. Carbon nanotubes are composed of carbon atoms linked in hexagonal shapes, with each carbon atom covalently bonded sp2 hybridized to other carbon atoms. Carbon nanotubes have diameters in the range of 1-100 nm and lengths up to several centimeters. High aspect ration ie length by dia ration. The electrical properties of a long and narrow carbon nanotube whether it is conducting or semiconducting are largely determined by its diameter and by the "rolling" angle between the main directions of the graphene lattice and the axis of the cylinder [23]. These parameters are constrained so that the type of nanotube can be described by two small integers. Most nanotube types are chiral, meaning that a tube cannot

be rotated and translated to match its mirror image [24]. Some other key features of CNTS apart from electrical properties are their mechanical and thermal properties such as - their mechanical tensile strength can be 400 times that of steel; they are very light-weight – their density is one-sixth of that of steel; their thermal conductivity is better than that of diamond; they have a very high aspect ratio greater than 1000, i.e. in relation to their length they are extremely thin.



Figure 1.4 Structure of Carbon nanotube

Chapter 2

LITERATURE REVIEW

2. Literature Review

Over the years a lot of research is being done on ferroelectric materials. Research in this area is driven by the market potential of next-generation memories, transducers, supercapacitors and energy storage material. All ferroelectrics are inherently dielectric materials. Among ferroelectrics, Barium Titanate is one of the most researched material, because of it's (i) high dielectric constant(\mathbf{k}), relative permittivity($\boldsymbol{\varepsilon}_{\mathbf{r}}$), and (ii) spontaneous polarization at room temperature. Barium titanate is an electrical ceramic with dielectric constant value as high as 7,000. Most common ceramic materials have dielectric constant less than 10, while others, such as titanium dioxide (TiO₂), have values between 20 and 70. With the advancement of nanotechnology and the discovery of Carbon Nanotubes by Dr. Sumio Ijima in 1991, a lot of research is being focussed on nanocomposites based on CNTs. CNTs are conducting, semiconducting or mix of both, which depends on its chirality. Both CNT & BaTiO₃ have peculiar and unique properties, which make them popular among researchers. Incorporating CNT in Barium Titanate may produce ideal material for many applications like EM wave absorption, high energy density capacitor, etc. Integrating CNT in inorganic BaTiO₃ matrix is challenging. Many interesting results have been bought up regarding the problems encountered during the synthesis of CNT Barium Titanate composite. This thesis brings into account the work of the predecessors in this field of research work.

2.1 Dielectric Materials

Dielectrics are non-conducting or insulating materials characterized by the poor conductor of electric current. Dielectric materials have the characteristic of holding an electrostatic charge while dissipating minimal energy in the form of heat. Examples of dielectric are Porcelain, Various Metal Oxides, Mica, Plastics, Glass and even dry air is also an example of the dielectric. A dielectric material can be any material that preserves charge without conducting it to a higher degree. Dielectric materials are used in a wide variety of applications, as electrical insulators, sensors, and circuit board components. The major use of dielectrics is in capacitors.

2.1.1 Dielectric Constant

The degree of polarizability or charge storage capability of a material is identified by the term dielectric constant or as relative permittivity.



Figure 2.1 Dieletric Placed within a Capacitor

When an electric field is applied to two flat plates of metal, one plate becomes positive and the other negative. The electric field causes polarization in the material in the space between the conductive plates. The relative dielectric constant (k') compares the polarizability of the material with that of the vacuum between the plates [7]: $\mathbf{k'} = \mathbf{k}$ material / \mathbf{k} vacuum (2.1)

2.1.2 Dielectric Loss

An ideal dielectric would allow no flow of electric charge, only a displacement of charge via polarization. Hence the current leads the voltage by 90°C; or out of phase by a quarter-cycle. Real materials always have some loss. The phase angle between the current and voltage is not exactly 90°C, the current leads the voltage by 90- δ , where δ is defined as the angle of lag. The angle of lag, δ , is the measure of the dielectric power loss. Power loss = $\pi f V_o^2 \varepsilon_r \tan \delta$ (2.2)

2.2 Nanomaterials

Nanomaterials are chemical substances or materials that have one physical dimension in the nanometric range[33]. These materials are developed to exhibit novel characteristics or enhanced physicochemical properties which are beneficial for different engineering applications, as compared to the same material in bulk form or without nanoscale features.

2.3 Composites

A composite material is a materials system made by combining two or more materials. Often those constituent materials have very different properties. The two/multiple materials work together to give the composite unique properties. The most significant point here is, in a composite system one can easily tell the different constituent materials as they do not dissolve or blend into each other (Unlike alloys). In a composite materials system, we have the host materials known as matrix and the secondary phase is called reinforcing phase.

2.4 Electrical Ceramic

Electrical ceramics are a group of advanced ceramic materials that are employed in a wide variety of electric, optical, and magnetic applications. In contrast to traditional ceramic products such as brick and tile, which have been produced in various forms for thousands of years, electroceramics are a relatively recent phenomenon. Examples of electro-ceramics include Zinc oxide for varistors, lead zirconium titanate (PZT) for piezoelectrics, barium titanate for capacitors, tin oxide as gas sensors, lead lanthanum zirconium titanate (PLZT) and lithium niobate for electro-optic devices. Table-2.1 summarizes the physical properties of some electro-ceramics required for these applications [32].

Material	Pronerties	Application
AlaOa BIN BaO	Low Permittivity High thermal conductivity	Packaging substrate
A1203, DIN, DEO	Low remnitrivity, ringh thermal conductivity	I ackaging substrate
BaTiO ₃	High Pertivity, High Break down Voltage	Capacitor
LiNbO ₃	High Piezoelectric Coefficients	Sensors, Piezo transducer
BaTiO ₃ (PTC)	Change of resistance with temperature	Thermistors
ZnO	Change of resistance with electrical field	Varistors
PLZT	Change of bifrienges with the applied field	Electro-optics
ZrO ₂	Ionic Conductivity	Gas Sensors
SnO ₂	Surface Controlled conductivity	Gas Sensors
Ferrites	Permeability, Coercive field	Magnets
PZT	Change of polarization with temperature	Pyroelectrics

Table-2.1: Examples of electroceramics, physical properties, and applications

2.4.1 Polarization in Electrical Ceramics

Ceramic materials that are good electrical insulators are referred to as dielectric materials. Although these materials do not conduct electrical current when an electric field is applied, they are not inert to the electric field (E). The field causes a slight shift in the balance of charge within the material so that the system acquires an electrical dipole moment (P) [7]. The dipole moment per unit volume is called **polarization**[29]. This moment is proportional to the electric field, E [28]. Figure (2.1): Shift in the distribution of charge in a ceramic insulator when it is placed in an electric field between two electrically conductive electrodes The polarization is always proportional to the applied field; thus $\mathbf{P} = \varepsilon_0 \chi_e \mathbf{E} \dots (2.3)$ Where: χ_e is the dielectric susceptibility. Since the dielectric susceptibility χ_e is equal to (ε_r -1), where ε_r is the relative permittivity, the polarization will be [29]: $\mathbf{P} = \varepsilon_0 \mathbf{E} (\varepsilon_r - 1) \dots (2.4)$ The field that a molecule in the interior of a dielectric situated between the plates of a charged condenser actually experiences is known to be larger than the applied field. This is related to the polarization which occurs within and on the surfaces of the dielectric. The actual field acting on the molecule is

therefore called the local field (Eloc). The dipole moment induced in a molecule by the local field is given by [29]: $\mathbf{P}_{mol} = \acute{\alpha} \mathbf{E}_{loc} \dots (2.6)$ Where: \mathbf{P}_{mol} represents its moment and $\acute{\alpha}$ is called the polarizability of the molecule. For dielectrics containing N molecules per unit volume, the total dipole moment or polarization is: $\mathbf{P} = N \acute{\alpha} \mathbf{E}_{loc} \dots (2.7)$ Substituting Equation (2.7) in Equation (2.5) gives: $(\mathbf{\epsilon}_{r-1}) = \mathbf{P}/\mathbf{\epsilon}_{0} \mathbf{E}_{loc} = N \acute{\alpha} \mathbf{E}_{loc} / \mathbf{\epsilon}_{0} \mathbf{E} \dots (2.8)$ There are several polarization mechanisms: Electronic polarization; orientation (dipolar) polarization; space charge polarization; and atomic or ionic polarization.



Figure 2.2: Types of polarization

2.4.1.1 Electronic polarization

Figure 2.2 shows the phenomenon of electronic polarization. Electronic polarization occurs in all dielectric materials. When an electric field, E, acts on an individual atom, the electrons surrounding each nucleus are shifted very slightly in the direction of the positive electrode and the nucleus is very slightly shifted in the direction of the negative electrode and the atom acquires a dipole moment P, so that: $P = \dot{\alpha} E$, where $\dot{\alpha}$ is the polarizability of the atom. As soon as the electric field is removed, the electrons and the nuclei return to their original distributions and polarization disappears. The displacement of charge is very small for electronic polarization, so the total amount of polarization is small compared to the other mechanisms of polarization [7], [28].

2.4.1.2 Orientation polarization

Figure 2.2 shows the phenomenon of orientation polarization, If the system is composed of heteronuclear (nonsymmetrical) molecules then the disposition of the individual atoms within the molecule may be such that the molecule itself has a permanent dipole moment. Examples are H₂O, HCl, CH₃Br, Hf, and C₂H₅(NO₂) [28]. For the H₂O, the covalent bonds between

hydrogen and oxygen atoms are directional such that the two hydrogen atoms that have a net positive charge are on one side of the oxygen that has a net negative charge. H2O is polar because the ions are arranged in a triangle (Figure 2.2-b) [28]. It is much more important in liquids and gases. Due to the randomizing effect of the thermal vibrations this type of polarization is more effective as the temperature is decreased and it gives rise to a dielectric constant, which is temperature dependent [28].

2.4.1.3 Atomic or ionic polarization

Atomic polarization involves displacement of atoms or ions within a crystal structure when an electric field is applied, the field will tend to stretch the bonds between the ions and this will change the moment of the molecule. A wide range of polarization effects is possible through this mechanism, depending on the crystal structure, the presence of a solid solution, and other factors [7], [28].

2.4.1.4 Space charge polarization

Space charges are random charges caused by cosmic radiation, thermal deterioration, or are trapped in the material during the fabrication process [7]. Polarization of Dielectrics is associated with constantly changing electric field, known as alternating current(ac). An alternating electric field is characterized by their frequency. The figure shown below, figure 2.3 is a polarization phenomenon vs frequency of the alternating field.

Dielectric Constant vs. Frequency



figure 2.3 Dielectric Constant vs Frequency plot

2.4.2 Piezoelectricity

Piezoelectricity is the ability of certain crystalline materials to develop an electrical charge proportional to the mechanical stress [32]. Polarization occurs in single crystals of some materials when a stress is applied, one side of the crystal derives a net positive charge and the

opposite side derives a net negative charge. Only crystals that are anisotropic with no center of symmetry are piezoelectric (there are 32 crystal classes, 20 of them are piezoelectric). Even these are not piezoelectric in all directions. The piezoelectric effect is reversible in that, piezoelectric crystals when subjected to an externally applied voltage, they change shape by a small amount [7]. The piezoelectric phenomenon has led to the widespread use of piezoelectric ceramics as transducers in ultrasonic devices, accelerometers, and sonar devices [7].

2.4.3 Pyroelectricity

Pyroelectric crystals are a special class of piezoelectric crystals. They contain within their crystal structure a pre-existing spontaneous polarization along at least one crystallographic direction, heating of the crystal results in mechanical deformation due to thermal expansion, which causes a change in the extent of polarization. Of the piezoelectric crystal classes, 10 are pyroelectric. Examples of pyroelectric crystals include würtzite, tourmaline, Rochelle salt, triglycine sulfate, BaTiO3. Most pyroelectric materials lose their pyroelectric behavior as the temperature is increased to a few hundred degrees.

2.4.4 Ferroelectricity

Ferroelectrics (ferroelectric materials) are a subclass of pyroelectric crystals, exhibiting spontaneous polarization; they retain a dipole even after an applied voltage has been removed. The crystal must be noncentrosymmetric and contain alternate atom positions or molecular orientations to permit the reversal of dipole and the retention of polarization after the voltage is removed [7]. However, every ferroelectric has a temperature point above which the material becomes substantially non-electric, i.e. dielectric, known as its Curie temperature [8]. A very strong field could lead to the reversal of the polarization in the domain, known as domain switching [45]. The key characteristic of a ferroelectric crystal is that the direction of the polarization can be reversed by application of an electric field and that hysteresis loops result. Figure 2.5 describes what happens in a ferroelectric crystal such as tetragonal BaTiO₃ when an electric field is applied. The ferroelectric domains are randomly oriented prior to application of the electric field, that is at E = 0 and the net polarization is zero ($P_{net} = 0$). As an electric field is applied, and upon increasing this electric field the domains begin to move in the BaTiO₃ and align parallel to the applied field. The polarization reaches a saturation value when all the domains are aligned in the direction of the field. If the electric field is reduced to zero, many of the domains will remain aligned such that a remanent polarization (**Pr**) exists. Interpolation of the line until it intersects the polarization axis gives a value Ps, which refers to the spontaneous polarization, [34]. If the electric field is reversed, the domain will switch direction. When enough domains switch, the domains in one direction balance the domains in the opposite direction and result in zero net polarization. This occurs for an electric field called the coercive field (-Ec). The continued increase in the negative electric field causes net polarization in the opposite direction, reaching point B where all the available domains are aligned [7], [34]. Maximum alignment of domains can be achieved by cooling the BaTiO3 crystal through the 120°C (cubic-to-tetragonal transition or Curie temperature) while an electric field is applied (this is referred to as polling). Ferroelectric behavior is dependent on the crystal structure.



Figure 2.4 Hysteresis Loop

Figure 2.5 shows the hysteresis loop of a ferroelectric material. The point to note here is the retentivity and Coercivity shown by these materials as shown in figure 2.4. Ferroelectrics have been categorized in the literature in different ways. One approach classifies them as soft or hard. Examples of soft ferroelectric materials are; Rochelle salt, some other tartarates, some sulfates, nitrates, and nitrites. Hard ferroelectrics include the oxides formed at high temperature. They are mechanically hard and are not water-soluble. Examples include BaTiO₃, KNbO₃, CdNb₂O₆, PbNb₂O₆, PbTa₂O₆, PbBi₂Nb₂O₉, and many others.



Figure 2.5 Change in the area under the hysteresis loop with temperature

2.5 Perovskites

Perovskite is any material with crystal structure like calcium titanium oxide or calcium titanate, with the chemical formula CaTiO₃. The mineral was discovered by Gustav Rose in 1839 and is named after Russian mineralogist Count Lev Alekseevich Perovski (1792–1856). All materials with the same crystal structure as CaTiO₃, namely ABX₃, are termed perovskites. These materials are a very stable structure, a large number of compounds have been studied

and synthesized, a variety of properties, many practical applications. Perovskite structure is known to accommodate most of the metallic ions of the periodic table [35]. Distortions in the symmetry of the perovskite structure result in the diverse physical properties making them useful in various industrial applications [35],[36]. As they are capable of holding a large number of oxygen vacancies, certain perovskite makes oxygen ionic conductors [37].

2.6 Barium titanate

The chemical formula for barium titanate is BaTiO₃. As a powder, it is white to grey in color and has a perovskite structure. It is soluble in many acids like sulfuric acid, hydrochloric acid, and hydrofluoric acid. It does not dissolve in alkalis and water. In the pure form, it is an electrical insulator. However, on doping with small amounts of metals, especially Scandium, Yttrium, Neodymium, Samarium, etc. it becomes semiconducting and it shows positive temperature coefficient of resistivity (PTCR) properties in the polycrystalline form. At the Curie temperature, BTO undergoes a phase change from tetrahedral to cubic. Single crystals of barium titanate exhibit a negative temperature coefficient of resistivity (NTCR). BaTiO3 also exhibits ferroelectric properties and is an excellent photorefractive material. Due to its PTCR properties, it is often found to be used as a thermal resistor e.g. in thermal switches. In an experimental study, the band gap of tetragonal BaTiO3 has been reported around 3.40 eV (indirect band gap). Barium titanate ($BaTiO_3$) is known to have many potential applications in the microelectronic field due to its high capabilities to enhance the performance of the capacitors and other energy storage devices. BaTiO3 has been reported to have a wide band gap around 3.4 eV from previous experimental studies by Hongwei Gao, J. C. (2011) et al. Barium titanate (A ions), which are large in size (~158 pm), occupy the corner sites while the titanate ions (B ions) which are small in size (~60 pm), located in the centers of the cube and oxygen anions are on the face-centers. BaTiO₃ is popular amongst researchers because as recorded by F Jona et al in 1993. The researchers have given some clear verdicts about BaTiO₃, Firstly, because it is chemically and mechanically very stable, secondly, because it exhibits ferroelectric properties at and above room temperature, and finally because it can be easily prepared and used in the form of ceramic polycrystalline samples. Ferroelectricity in this compound is known to be highly sensitive to structure and hence becomes the cause of interest in materials with ABO₃ structure for practical applicability [Nalwa, 1999; Cross and Newnham, 1987]. BaTiO3 is also the first ferroelectric material to display a paraelectric high-temperature phase, having the highest symmetry i.e. centrosymmetric. This paraelectric phase is also called as the prototype phase. BaTiO3 is also polymorphic as it is found to have more than one ferroelectric phase [Nalwa, 1999; Gopalan et al., 2007]. The critical temperature above which BaTiO₃ loses its ferroelectric property is known as Curie temperature (T_C) [Kasap, 2007]. Below T_C BaTiO₃ is spontaneously polarized, and this spontaneous polarization is accompanied with the crystal structure distortion due to the displacement of Ti ion [Kasap, 2007]. Also, the ease with which BaTiO₃ can be switched back and forth between different ferroelectric phases led to scientific and technological interest in it. These ferroelectric instabilities arise from the covalent hybridization between Ti and O ions [Sanna et al., 2011]. Figure 2.7 shows the unit cell structure of BaTiO₃, its ferroelectric transitions and the phase diagram of BaOTiO₂ system [Moulson and Herbert, 2003; Rase and Roy, 1955; Avrahami, 2003; Lee et al., 2007].



Figure 2.6 Phases of Barium Titanate



Figure 2.7 Cubic to Tetragoanl transformation of BaTiO3

The wide range of applications as multilayer ceramics capacitors (MLCC), piezoelectric sensors, transducers, actuators, non-volatile ferroelectric random access memories (FRAM), dynamic random access memories (DRAMs) electro-optic devices and positive coefficient of resistance (PTCR) thermistors makes BaTiO₃ one of the highly desired electroceramic of the various known ferroelectrics [Kumar et al., 2009; Parveen et al., 2009; Mahajan et al., 2009; Gene, 1999. Also, the simple crystal structure, high stability, extremely high dielectric constant at the transition temperature, low leakage current, and anisotropic optical behavior adds up to the importance of BaTiO₃ [Sabina, 2001].

2.6.1 Synthesis of BaTiO₃

Barium Titanate is synthesized by multiple methods. Synthesis and sintering techniques determine the property of the produced final product. So it is imperative to study the different routes and techniques and underline the pros and cons of each route. Some of the routes of Barium Titanate synthesis are (i) solid-state reaction method, (ii) Hydrothermal synthesis, (iii) Coprecipitation Method, (iv) Mechanochemical Method, (v) Spray Drying and Roasting, (vi) Sol-Gel Method method

2.6.1.1 Solid-state reaction method

Solid solution ceramic samples are synthesized by mixing two or more solid compounds. The characteristics of starting constituents are retained and the desired mixture is formed. Basically, solids do not react at room temperature and hence, in order to complete the reaction, they are heated at higher temperatures. Synthesis of ceramic powders by the conventional solid-state reaction method and repeated heating with the intermediate mechanical or hand-grinding process is almost always essential to produce a single-phase powder to attain chemical homogeneity. Reaction rate increases due to the increase in the surface area hence, fine-grained

precursors are used., the grinding operation is performed which helps in reducing the particle size. Process of reducing the size of particles affects the homogeneity and purity of the material. Large scale production is frequently based on solid-state reactions of mixed powders BaCO3 and TiO2 at high temperatures [61]. According to Pavlović et al.[25], the following reactions sequence was proposed:

 $BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2 \dots (2.9)$ $BaTiO_3 + BaCO_3 \rightarrow Ba_2TiO_4 + CO_2 \dots (2.10)$ $Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3 \dots (2.11)$

Advantages of Solid State preparation of BaTiO3 are low production cost and the scalability on mass production. Disadvantages are The particle size of the initial powder and the homogeneity are very important factors in the determination of the reaction mechanism, mechanical processing of powders should be done carefully, High Temperature reaction, Comparatively slow as compared to Sol-Gel synthesis, Physically the powders of Oxides of Titanium and Barium Carbonate are mixed, sintered then grinded and again fired to high temperature, may lead to formation of unnecessary products, This method, leads to large BaTiO3 particles (usually above 1 micrometer) with wide grain-size distribution, irregular morphologies and impurities, which may result in poor electrical properties and reproducibility of sintered ceramics.

2.6.1.2 Hydrothermal Synthesis

Hydrothermal synthesis is generally defined as crystal synthesis or crystal growth under high temperature and high-pressure water conditions from substances which are insoluble in ordinary temperature and pressure. The combined effects of solvent, temperature, and pressure on the ionic reaction, stabilizes desirable products, inhibiting the formation of undesirable compounds such as BaCO3. Hydrothermal synthesis of BaTiO3 is done in a single step without using sophisticated apparatus or expensive reagents have also been achieved.

2.6.1.3 Coprecipitation Method

The coprecipitation principle is very simple. A number of different ions, which are normally dissolved in water, are simultaneously precipitated. In most cases, finely dispersed intermixtures of insoluble hydroxides or carbonates, etc., are formed. Amongst all the wet chemical synthesis techniques, coprecipitation method is very useful as it avoids the primary preparation of solid or gel precursor [Buscaglia et al., 2004; Her et al., 1996; Kumar, 1999; Leoni et al., 1996; Viviani et al., 2003]. Coprecipitation is a useful and plain technique by

which homogeneous compounds can be made, due to the mixing of constituent ions at a molecular level under a controlled environment, [42], [41]. Depending on the reaction conditions fine uniform monocrystalline particles of 5 - 10 nm in size can be produced.

2.6.1.4 Mechanochemical Method

Mechanochemical methods deal with chemical transformations induced by mechanical energy, such as compression, shear, or friction. according to IUPAC, a mechano-chemical reaction is a 'Chemical reaction that is induced by the direct absorption of mechanical energy' and with a note 'Shearing, stretching, and grinding is typical methods for the mechano-chemical generation of reactive sites, usually macroradicals, in polymer chains that undergo mechano-chemical reactions'. Heat is released during this process, initiating solid-state reaction due to the formation of new surfaces and increasing concentration of crystal lattice defects. This is accompanied by an increase in surface energy of the particles, increasing the reactivity of the starting mixture and lowering the sintering temperature. [42],[43].

2.6.1.5 Sol-Gel Method

The sol-gel process is a change from the liquid state to gel state through polycondensation reactions. The term sol-gel was coined in the late 1800s. It is a low-temperature method ("sol" for solution) using chemical precursors that can produce ceramics and glass with higher purity and better homogeneity than high-temperature conventional processes. Sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. Typical size few nanometers. A gel consists of a three-dimensional continuous network of the sol particles, which encloses a liquid phase. The sol-gel process is divided into two types 1) Collodial and 2) Polymeric. In a colloidal gel, the network is built from the agglomeration of colloidal particles. In a polymer gel, the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. The sol-gel processing technique is been used to produce a wide range of ceramics (mostly oxides) of different physical forms, such as powders, fibers, coatings, thin films, monoliths, composites, and porous membranes. Organic/inorganic hybrids, in which a gel (usually silica) is impregnated with polymers or organic dyes to provide specific properties, also can be made. Sol-gel techniques have been successfully applied to a number of monocomponent systems, like Al₂O₃ or SiO₂. In multi-component systems, problems may arise from the fact that certain compounds, as for instance the ions of alkaline earth elements, do not form polymer gels. Colloidal particles are much larger than nanoparticles. However, upon mixing with liquid colloids appear hazy while the nano range molecules always look clear. In this process evolution of networks occurs, through the formation of colloidal suspension (sol) and gelation to form a network in the continuous liquid

phase (gel). The precursor for synthesizing these colloids consists of ions of metal alkoxides and alkoxysilanes. For the synthesis of Barium Titanate using sol-gel method barium acetate and titanium isopropoxide is usually taken as the starting material. These are reacted to form a sol and then gelation takes place, on drying and heat treatment it gives amorphous oxide upon further heat treatment crystallization is induce [38], [39], [40]. Advantage of synthesis of BaTiO₃ by solgel are (i)Very high purity achievable (99.999), (ii)Excellent control of the composition of the resulting powders,(iii) Low-temperature process (around 80-100 degree Centigrade), (iv) Fast as compared to Solid State route of synthesis, (v) Precise control over the doping level is also easier in this process.

The disadvantages are (i) strict control of reaction temperature, (ii) long synthesis procedures, (ii) barium & titanium alkoxides require an inert atmosphere.

Sol-gel formation occurs in four stages namely - i)Hydrolysis ii)Condensation iii) Growth of particles iii)Agglomeration of particles

Hydrolysis:	$-M-OR + H_2O$ —	\rightarrow -MOH + ROH
Condensation:	-M-OH + XO-M-	\longrightarrow -M-O-M- + XOH

2.7 Carbon Nano Tubes

Carbon nanotubes (CNTs) are a group of nanomaterials that consists of a two-dimensional hexagonal lattice of carbon atoms, bent and joined in one direction so as to form a hollow cylinder. Kaushik, Brajesh Kumar, Majumder, Manoj Kumar in their book Carbon Nanotube-Based VLSI Interconnects write elaborately about the Carbon nanotubes (CNTs), and how they are made by rolling up of a sheet of graphene into a cylinder. These nanostructures are constructed with length-to-diameter ratio of up to (1.32×10^8) :1 [27] that is significantly larger than any other material. Since carbon nanotubes (CNTs) were discovered in 1991 by Iijima, they have been the subject of intense research activity because of their unusual properties. A carbon atom can form various types of allotropes. In 3D structures, diamond and graphite are the allotropes of carbon. Carbon also forms low-dimensional (2D, 1D or 0D) allotropes collectively known as carbon nanomaterials. Examples of such nanomaterials are 1D carbon nanotubes (CNTs) and 0D fullerenes. In the list of carbon nanomaterials, graphene is known as 2D single layer of graphite. The *sp2* bonds in graphene are stronger than *sp3* bonds in diamond that makes graphene the strongest material [26]. The lattice structure of graphene in real space consists of a hexagonal arrangement of carbon atoms as shown in Fig. 2.8 a. Isolated

carbon atoms have four valence electrons in its 2*s* and 2*p* atomic orbitals. While forming into graphene, three atomic orbitals of the carbon atom, 2*s*, 2*px*, and 2*py*, are hybridized into three *sp*2 orbitals. These *sp*2 orbitals are in the same plane while the remaining 2*pz* is perpendicular to other orbitals as shown in Fig. 2.8b[26]. The σ bonds between the adjacent carbon atoms are formed by the *sp*2 hybridized orbitals, whereas the 2*pz* orbitals form the π bonds that are out of the plane of graphene [46].



Figure 2.8 Graphene Sheet

As their name suggests, the diameter of a nanotube is in the order of few nanometers, while they can be up to 18 centimeters in length[46]. A CNT can carry current density in excess of 4 $x10^9$ A/cm², which can enhance the electrical performance as well as eliminate electromigration reliability concerns that plague current nanoscale Cu interconnects [49].

2.7.1 Structure and property of Carbon Nanotubes

To understand the crystal structure of CNTs, it is necessary to understand their atomic structure. Both CNTs and GNRs (graphene nanoribbons) can be understood as structures derived from a graphene sheet, shown in Figure 2.8 A graphene sheet is a single layer of carbon atoms packed into a 2D honeycomb lattice structure. CNT, considered as rolled-up graphene sheet, have the edges of the sheet joint together to form a seamless cylinder. The dashed arrows in Figure 2.9 a, b show the circumferential vector *C*, which indicates the rolling up direction for CNT. The vector is defined as $C = n1 \ a1 + n2 \ a2$ where a1 and a2 are the lattice vectors of graphene and n1 and n2 are the chiral indices. The chiral indices (n1, n2) uniquely defines the chirality or the rolled-up direction of the graphene sheet. Depending on the chiral indices (n1, n2),







Figure 2.10 SWNCT, DWCNT, and MWCNT

CNTs can be classified to zigzag and armchair structures as shown in Figure 2.9 a, b, respectively. For armchair CNTs, the chiral indices n1 and n2 are equal while for zigzag CNTs, n1 or n2 = 0[47]. For other values of indices, CNTs are known as chiral. Depending upon their different structures, CNTs can exhibit metallic or semiconducting properties. By satisfying the condition n1 - n2 = 3i (where *i* is an integer), the armchair CNTs are always metallic, whereas zigzag CNTs are either metallic or semiconducting in nature [46], [47]. Statistically, a mix of CNTs will have 1/3rd metallic and 2/3rd semiconducting chiralities. Depending on the number of concentrically rolled-up graphene sheets, CNTs are also classified to single-walled (SWNT), double-walled (DWNT), and multiwalled CNTs (MWNT) as presented in Figure 2.10

2.7.2 Electrical Conductivity of Carbon Nano Tubes

A metallic CNT can be considered as a highly conductive material. Chirality, the degree of twist of the graphene sheet, determines the conductivity of CNT interconnects. Depending on the chiral indices, CNTs exhibit both metallic or semiconducting properties. The electrical conductivity of MWNTs is quite complex as their inter-wall interactions non-uniformly distribute the current over individual tubes. However, a uniform distribution of current is observed across different parts of metallic SWNT [50]. The measured resistivity of the SWNT ropes is in the order of 10–4 Ω cm at 27 °C, indicating SWNT ropes to be the most conductive carbon fibers [51]. Each carbon atom in a single sheet of graphite is connected via a strong chemical bond to three neighboring atoms. The elastic modulus of SWNTs is much higher than steel that makes them highly resistant. CNTs are extremely useful as probe tips for high resolution scanning probe microscopy. Although, the current Young's modulus of SWNT is about 1 TPa, a much higher value of 1.8 TPa has also been reported (Hsieh et al. 2006). For different experimental measurement techniques, the values of Young's modulus vary in the range of 1.22 TPa-1.26 TPa depending on the size and chirality of the SWNTs [51]. It has been observed that the elastic modulus of MWNTs is not strongly dependent on the diameter. Primarily, the moduli of MWNTs are correlated to the amount of disorder in the nanotube walls

(Forro et al. 2002). Due to their high thermal conductivity and large in-plane expansion, CNTs exhibit exciting prospects in nanoscale molecular electronics, sensing and actuating devices, reinforcing additive fibers in functional composite materials, etc. Recent experimental measurements suggest that the CNT embedded matrices are stronger in comparison to bare polymer matrices [49]. Therefore, it is expected that the nanotube may also significantly improve the thermo-mechanical and the thermal properties of the composite materials. One of the exciting properties of CNTs is the high aspect ratio, inferring that a lower CNT load is required compared to other conductive additives to achieve similar electrical conductivity. Carbon nanotubes and CNT composites have been emerging as perspective absorbing materials. The absorption frequency range of SWNT-polyurethane composites broaden from 6.4–8.2 (1.8 GHz) to 7.5–10.1 (2.6 GHz) and to 12.0–15.1 GHz (3.1 GHz) [27].

The above literature about chirality of CNTs can be summarised as the following table: Table 2.2 Chirality and Electrical Conductivity of CNT

Chirality	n1,n2 chiral indices	Electrical Property
Zig-zag	n1≠0 & n₂=0	1/3 rd metallic 2/3 rd semi-
		conducting
Arm-chair	$n_1 = n_2$	Conducting (Metallic)
Chiral	For other values of indices	Semiconducting

2.8 Advancements and review of previous work

To be compatible with applications concerning current existing technology, Researches in BaTiO₃ materials are being focussed on its properties which were explored via various means. Among these, increase in purity of the product with minimum energy consumption, synthesis of BaTiO₃ powder in nano-dimension, reduction in heat treatment temperature, reduction of the cost of synthesis, doping with different periodic elements and also with known compounds to modify its properties in order to achieve the desired result are exploited the most.

Mazdiyasni et al. [4,5] used barium isopropoxide derived from high-purity Ba metal, whereas Flaschen [6] chose Ba(OH)₂ as a starting material. Ritter et al. [9] studied the alkoxide-based synthesis of phases in the system BaO-TiO₂. Phule et al. [10] presented a comparison of different starting materials used in BaTiO₃ synthesis.

Lujun Yu et al, 2016[59], Incorporated Barium Titanate-CNT in polyaniline for strengthening electromagnetic absorption capability. Employing an easy and flexible method consisting of the sol-gel route, in situ polymerization, and subsequently developed a mechanical method to prepare the barium titanate/carbon nanotubes incorporated polyaniline (CNTs/BaTiO3/PANI or CBP) ternary composites. Carbon nanotubes (CNTs) can be a promising material for reduction of electromagnetic radiations (EM) due to the combined lightweight and remarkable

mechanical and electronic properties [64–66]. However, they reported that the good conductivity of carbon nanotubes used as a microwave absorbing material has the shortcoming of poor impedance matching. carbon nanotubes combination with a dielectric material also can improve the impedance matching and induce losses like capacitor effect, antenna effect, polarization effect, and so forth. Barium titanate (BaTiO3) [67] represents one of the most studied dielectric materials due to its high dielectric constant, positive temperature coefficient, and nonlinear optical properties.

Huang et al. [69] synthesized BaTiO3/MWCNTnanocomposites with the mass ratio BaTiO3: MWCNT = 25: 1 which exhibited excellent absorption properties. Zhu et al. [69] found that MWCNT covered with BaTiO3 possessed better microwave absorbing properties than the pure MWCNTs in the frequency range 11–15GHz. Lujun Yu et al used functionalized CNT with hot concentrated HNO₃ and then added into BaTiO₃ sol system under sonication for 1 h. The Barium Titanate Sol was prepared using butyl titanate (Ti(OC₄H9)₄), Barium acetate (Ba(CH₃COO)₂). Their work illustrated that Barium titanate/carbon nanotubes incorporated in polyaniline composites with 3D conductive network structure were successfully prepared by an easy and flexible method, which exhibit excellent microwave absorbing properties. The good dielectric properties and high impedance matching of CBP composites are due to the presence of CB and PANI, as well as the synergistic effect and geometrical effect due to the microstructure which collectively contributes towards the outstanding performance. They concluded that it is reasonable to believe that Barium Titanate CNT and PANI composite has the potential for making futuristic microwave absorbers.

Osman, KOLTHOUM ISMAIL[31], in his thesis synthesis and characterization of BaTio3 ferroelectric material, synthesized BaTiO3 by using the solid-state reaction method, starting with two different precursors each having 1:1 molar ratio; the BaCO3/TiO2. And reported that, the formation of BaTiO3 proceeds through a direct reaction between BaCO3 and TiO2, not through the decomposition of BaCO3 to BaO neither through the formation of Ba2TiO4 intermediate phase using characterization techniques like DTA-TG, XRD, and the thermodynamic analyses. The significant outcome he reported was that the tetragonality of Barium Titanate increases with the sintering temperature.

Xu Huang et al[68], synthesized a series of novel BaTiO3-MWCNTs core/shell heterostructure via the solvent-thermal method. Due to rapid development in telecommunication, navigation, voyage and an increasing number of electronic devices Electromagnetic (EM) interference problem has become increasingly serious. It is noteworthy that EM interference can not only cause an interruption in the electronic system but also lead to potential harm to human health

[70],[71]. Hence, they studied EM wave absorbing materials and extensively investigated to solve the EM interference problems. They combined inorganic BaTiO3 with MWCNTs, both the materials possess certain EM wave absorption property. In order to prepare a product with better EM absorb property through synergistic enhancement effect, they adjusted the molar ratio of BaTiO3 and MWCNTs, BaTiO3-MWCNTs heterostructure with different morphologies and EM performance was obtained. The microwave absorption properties of the as-synthesized products were shown. Based on the theory of transmission line, the reflection loss (RL) of BaTiO3-MWCNTs heterostructure was simulated [72],[73].

J. G. Sriram et al[56] in Characteristics of BaTiO3–carbon nanotube composite synthesized by mechanical milling, synthesized Barium Titanate CNT composite using mechanical milling. Then the nanocomposite was characterized by X-ray diffraction, SEM, thermal gravimetric analysis and LCR meter. The thermal stability of the composite was lower than that of pure barium titanate, which was attributed to the presence of trace amounts of sodium dodecyl benzene sulphonate. BT based composites have focused on the addition of conductive metal fillers such as Ag and Ni in a BT based matrix or BT nanoparticles dispersed in a polymer matrix10 and only limited published work focuses towards the synthesis of CNT–BT based composites. The dielectric constant of the composite was 69.23% greater than that of the pure BT which could be explained based on Maxwell–Wagner polarisation due to the heterogeneous system. This increase in dielectric constant makes these BT–CNT composites ideal for capacitor applications.

Benhui Fan [57], Dielectric properties of carbon nanotube-BaTiO₃ hybrids reinforced PVDF composites. Materials, Université Paris-Saclay, 2015, dispersed CNT in barium titanate (BT) polymer matrix and reduced the percolation threshold of the composite. His research work aimed to achieve the high dielectric performance of composites via designing fillers with the favorable structure as well as comprehensively study interactions between CNT and semi-crystalline polymer matrix(PVDF). His thesis work showed the unique structure of H-CNT-BT improves CNT's dispersion in the PVDF matrix and consequently reduces the percolation threshold. The experimental results showed that not all hybrids have a positive effect on CNT's dispersion in PVDF. Dielectric property highly depends on the hybrid structure because the percolation threshold is largely affected by the way of BT particle's existence. By the comparison and analysis for three composites prepared by the same processing way and with the same BT and CNT's volume fraction but different BT-CNT structures, we find H-CNT-BT/PVDF has the highest dielectric property due to the unique structure of H-CNT-BT which effectively reduces the percolation threshold.

Qing Huang et al[58], in Sintering and thermal properties of multiwalled carbon nanotube-BaTiO3 Composites, studied the sintering and thermal properties of MWCNT-Barium Titanate composite. Firstly, they immobilized nanosized rutile titania on MWNTs. Then, this titania-MWNTs hybrid material was transformed to BaTiO3-MWNTs hybrid material via a hydrothermal approach. Finally, the synthesized BaTiO3-MWNTs hybrid material and nanosized tetragonal phase BaTiO3 powders with sizes smaller than 112 nm and Ba/Ti mol ratio of 1.001, were weighed according to precalculated proportion (0.1 wt%, 0.5 wt%, 1 wt%, and 3 wt%), and then mixed without dispersant by ball milling in ethanol solution for 24 h. The obtained mixed slurry was dried at 100 °C for 12 h and further dehydrated in a vacuum oven 60 °C for 12 h to get MWNTs-BaTiO3 composite powders. Dry composite powders were ground and sieved using a 200 mesh sieve before use. Spark plasma sintering technique was used, They applied pressure of 35 MPa at the beginning of the sintering process and released after the annealing duration. The annealing time was set at 0–5 min. The sintering temperatures were set at 800–1000 °C at 50 °C intervals. The heating rate was set at 300 °C per minute. They reported the sintering properties and thermal properties of MWNT-BaTiO3 composites fabricated via SPS method. The microstructures of composites sintered under different conditions and with varied content of CNTs are observed through SEM microscopy. Interestingly, the densification temperature of MWNT-BaTiO3 composites is markedly decreased by the addition of MWNTs. In addition to the electrical property, the thermal properties of MWNT-BaTiO3 composites including specific heat capacity, thermal diffusivity, and thermal conductivity are also principally investigated. Although the specific heat capacity increases after adding CNTs, the thermal diffusivity and thermal conductivity both decrease. Besides the reduced BaTiO3 grain size, the interfacial thermal barrier between CNTs and BaTiO3 matrix is also regarded as playing a crucial role in determining the thermal conductivity of bulk composites.

Aga, Zubeda Bi H[44]. In Synthesis and Characterization of Nano-Sized Pure and Doped Barium Titanate Powders Prepared by Sol-Gel Emulsion Technique, studied the electrical properties of pure and doped barium titanate. Doping helped in tailoring the properties of pure BaTiO3, the dopant ion strongly affected the structure and properties. Sr, La, Ce, Mg, Li, and K were the chosen dopants in that study. Strontium doped Barium Titanate is known to decrease T_C towards room temperature and possess non-linear dielectric behavior, having various application as electromechanical sensors, tunable filters, phase shifters, high-Quality factor resonators, etc. Lanthanum being a donor induces semiconductivity giving rise to PTCR effect in BaTiO3 to be used as a PTCR thermistor. La and Ce doping are also known to decrease

 T_C towards room temperature. The dielectric properties of these dopants have led to their use in capacitors. Magnesium as an acceptor was used to modify the PTCR effect in BaTiO3 and also reduce TC towards room temperature. Lithium and Potassium doping in BaTiO3 was only studied for its structural properties and in modified Barium Titanate for its PTCR effect.

Gan Jet Hong Melvin et al[18], studied Barium titanate nanoparticles fabricated using the solgel method, and then immobilized onto the carbon nanotubes (CNTs) surface to fabricate heterogeneous barium titanate-carbon nanotube (Barium Titanate-CNT) nanocomposites. They studied the electromagnetic wave absorption ability, they recorded that the absorption capacity of the nanocomposite system increased as the weight fraction of the CNT in the Barium Titanate-CNT nanocomposite system increased. The percentage of CNT in the Barium Titanate-CNT was 30 wt.%.. The relationship between conductivity and EM wave absorption properties was also discussed.

Sahu, Jyoti Prakash[20]. Prepared and Characterized Carbon Nanotubes Barium Titanate Composites. Carbon Nanotubes Barium Titanate composites were successfully prepared through grinding and agate mortar with varying concentrations of CNTs. The XRD results of CNT-Barium Titanate composite showed that the graphitic peaks of the composites were subdued because of higher concentration of Barium Titanate however the reason was yet to be ascertained. The SEM images confirmed the presence of Carbon Nanotubes with the varying percentage in the prepared composites. From the electrical resistance measurements, it was observed that the resistance decreases with increasing Carbon Nanotubes concentration.

Chapter 3

OBJECTIVE

3. Objective

The main objective of this research is to synthesize and characterize the sol-gel derived Barium Titanate-CNT composites using organometallic precursors in order to unravel the effect of homogeneously dispersed CNT on Barium Titanate matrix for developing a high-performance composite material.

Chapter 4

EXPERIMENTAL
4. Experimental

4.1 Starting Materials

- 1. Barium Acetate Ba[CH₃COO]₂, 99.00% extra pure, Loba
- 2. Titanium(IV) Isopropoxide Ti[OCH(CH₃)₂]₄ 97%, Sigma Aldrich
- 3. Ethyl Alcohol CH₃CH₂OH 99.9% v/v, of Hayman.
- 4. Acetic acid CH₃COOH, glacial 100% of Merck.
- 5. Distilled Water H₂O, of Merck.
- 6. -COOH Functionalised Multi-walled Carbon Nano Tubes, 98% pure
- 7. Sodium Dodecyl Sulfate, of Merck.

4.2 Procedures

Table 4.1: Batch composition chart

Batch	Barium Titanate	CNT (wt%)
number	(wt%)	
1	100	0
2	99.95	0.05
3	99.85	0.15
4	99.7	0.3

4.2.1 Preparation of BaTiO₃ Sol

Titanium isopropoxide and Barium acetate were used as precursors to prepare the BaTiO₃ powder by sol-gel method. To make Barium acetate precursors we mixed Acetic acid and Distilled water in a magnetic stirrer for 10 min and then added Barium Acetate using a spatula slowly and stirring for 30 min. To make Titanium isopropoxide precursor we mixed Acetic Acid and Ethyl Alcohol in a magnetic stirrer for 10 min then added Titanium isopropoxide and stirred for 30 min. After that two individual solutions were mixed slowly at a constant rpm of 350. The recorded pH was 3 at a temperature of 40°C. A watch was kept on the temperature of the precursor mixture and stirred for 2 hours at a constant rpm. Poured the precursor in a clean beaker and were aged for natural drying of gel formation for about four weeks. Then dried it at a temp of 110°C for overnight(24 hours) in a drier, after that pulverized it into powder form.



Figure 4.1: Synthesis schematic of BaTiO3 Sol 4.2.2 Preparation of CNT dispersed BaTiO3 Sol

Titanium isopropoxide and Barium acetate were used as precursors to prepare the $BaTiO_3$ powder by sol-gel method. To make Barium acetate precursors we mixed Acetic acid and Distilled water in a magnetic stirrer for 10 min and then added Barium Acetate using a spatula slowly and stirring for 30 min. To make Titanium isopropoxide precursor we mixed Acetic Acid and Ethyl Alcohol in a magnetic stirrer for 10 min then added Titanium isopropoxide and stirred for 30 min. After that two individual solutions were mixed slowly at a constant rpm of 350. The recorded pH was 3 at a temperature of 40°C. Kept watch on the temperature of the precursor mixture and keep stirring for 2 hours at a constant rpm. Poured the precursor in a clean beaker and the desired weight % of CNT was mixed along with SDS surfactant, then Ultrasonicated for 15 minutes. Carbon Nano Tube used in our project had the following physical properties as specified by the manufacturer: (i) –COOH functionalized, (ii)Diameter 15-20 nanometer, (iii), (iv)Length 20 micrometer, (v) Metallic impurity contents < 2%, (vi) Bulk Density 0.1-0.06 g/cm³. CNTS due to the high specific surface area have the tendency to form agglomerates. For proper dispersion of CNTS in a sol system, we needed a surfactant which will work a dispersing agent. According to the DLVO (Derjaguin, Landau, Vervey, and Overbeek), theory particles in aqueous media can be agglomerated when van der Waals attraction is greater than electrostatic repulsion (Verwey et al., 1999; Derjaguin and Landau, 1941). The van der Waals forces of attraction between MWCNTs are very high, so they agglomerate. This was observed during our process. We tried dispersing MWCNT in the

Barium Titanate sol without using SDS, but MWCNTs agglomerated and settled in the Test Tube within minutes of vigorous Ultrasonication in an Ultra Sonicator bath. The MWNTs are microporous. A dispersion is a system in which distributed particles of one material are dispersed in a continuous phase of another material. The two phases may be in the same or different states of matter. Figure 4.9 shows the agglomeration of MWCNT in sol. Then the mixture of Sol and CNT was aged for natural drying of gel formation for about four weeks. Then dried it at a temp of 110°c for overnight(24 hours) in a drier, after that pulverized it into powder form.



Figure 4.2: Synthesis schematic of CNT dispersed BaTiO₃ Sol

4.3 Calcination

The Solid mass obtained after drying was made into powder using agate, the BaTiO3 powders were heat treated at temperatures of 400°C, 500°C and 700°C in the furnace. The heat treatment temperatures were fixed to 400°C, 500°C and 700°C, after carefully analyzing the DTA results. A constant heating rate was maintained for every calcination temperature at 5°C/minute.

4.4 Some Experimental Photographs



Figure 4.3 Stirring of Barium and Titanium precursor



Figure 4.4 Stirring of the sol



Figure 4.5 Transparent BaTiO₃sol





Figure 4.6 Ultrasonication of CNT dispersed BaTiO₃ sol

Figure 4.7 Dried samples



Figure 4.8 Calcination in furnace

Figure 4.3-4.8 shows the different steps of our synthesis. Figure 4.3 shows stirring of Barium and Titanium precursors in Distilled water and Alcohol respectively, with proper temperature setting and adding acetic acid to maintain pH. Figure 4.4 shows stirring the sol for 2 hours. Figure 4.5 shows freshly prepared sol. Figure 4.6 shows adding MWCNTs in the sol and ultrasonication. Fig 4.7 shows the dried xerogel. Fig 5.8 shows heat treatment of the xerogel powders contained in alumina crucibles in a muffle furnace with a soaking time of 2 hours. We added Sodium Dodecyl Sulfate as a surfactant to disperse –COOH functionalized MWCNT in Barium Titanate Sol. We added twice weight of SDS in our Sol with respect to CNT. First, the SDS was added to Sol and ultrasonicated in 40° C hot water bath for 10 mins. After the SDS got homogenously mixed in the sol system, We added MWCNT, then Ultrasonicated for 15 minutes, at 40°C bath.



Figure 4.9 Agglomeration of CNT in BaTiO₃ sol before adding SDS

Figure 4.9 and figure 4.10 shows the effect of dispersing CNT in Barium Titanate sol by not adding SDS and by adding SDS.

4.5 Sample Characterization

4.5.1 Fourier Transform Infrared (FT-IR) Study

Infrared spectra in the range 4500–400 wavenumber (cm–1) using a Fourier transform infrared spectrometer (FTIR, Shimadzu IR Prestige-21) in transmittance mode. The sample discs for FTIR studies were prepared by mixing 2.5gm of solid sample and 250gm of KBr. The mixed powders were transferred into a steel die of 1cm and subjected to a pressure of 10tones for 2min to obtain the disc. These discs were then placed in the sample holder of the instrument for analysis purpose.



Figure 4.11 Typical picture of a FTIR Machine

4.5.2 Differential Thermal Analysis study

Thermal behavior of the Bacth 1 and Batch 3were investigated by differential thermal analysis (DTA) using Okay Instruments 10.8 Differential Thermal Analyser 15000°C instrument in an oxidizing atmosphere. The xerogel of Solgel derived Batch 1 and the Batch 3 were characterized. Two samples weighing 0.100mg each was loaded in a ceramic sample holder. The xerogels were subjected to thermal decomposition from room temperature to 1000°C. Data were recorded and the heating step size was 10°C min–1 in air. Platinum crucible with alpha alumina powder was used as a reference.

4.5.3 X-Ray Diffraction (XRD) Study

Phase identification, purity, relative crystallinity and crystallite size of all the samples were obtained at room temperature using X-ray diffractometer (Rigaku, Ultima III). Diffraction patterns were obtained using Cu K α radiation = 1.54Å at 40kV and 30mA with a scanning rate of 4°/min in the 2 θ range from 10 to 80°. XRD patterns are fitted using Savitzky –Golay smoothening for phase determination.



Figure 4.12 Typical picture of a Xray diffraction machine

4.5.4 Scanning Electron Microscopy

Surface morphology of the synthesized composite, heat treated at two different temperature (500°C and 700°C) were analyzed using scanning electron microscopy (FEI quanta FEG 450) operating at 20.0 kV. The samples were dispersed on carbon tape pasted on a stub. Prior to imaging the samples were coated with Palladium using an ion sputtering instrument for better

conduction.



Figure 4.13: Typical picture of a scanning electron microscope

4.5.5 Raman Spectrometry study

To study the vibrational, rotational and other low frequency transitions in the prepared samples of batch 1, batch 4 and the functionalised MWCNT Raman spectrometric study was performed. The samples were scanned from 100 cm^{-1} to 2000 cm^{-1} range.

4.5.6 UV-Vis Spectrometry study

The band gap analysis of our samples was done using UV-Vis spectrophotometer machine, model Shimadzu UV 3600. The solid samples were analyzed in the wavelength range of 200-2200 nm range. The samples were loaded in a quartz cuvette and analyzed in the above-said wavelength range. Infrared spectroscopy can be used to analyze solid, liquid, or gas samples. Here, we discuss the measurement of solids, particularly powder samples, by the diffuse reflection method. The bandgap estimation was done using the Kubelka-Munk model.



Figure 4.14 Typical picture of a UV-Vis machine

Chapter 5

RESULTS AND DISCUSSION

5. Results and Discussion

5.1 Fourier Transform Infrared Spectroscopy Analysis

Serial	Wave Number	Reference	Remark
Number	(cm ⁻ 1)	wave	
		Nuber(cm ⁻	
		¹)[52],[79],[78]	
01	476/464/473/455	470	Ti-O Stretching Vibration
02	584/528	539	BaTiO ₃
03	650/667/676/681	658	Ti-O Stretching Vibration
04	788	800	M-O bands like Ti-O or Ti-O-Ti
05	933	936	O-Ti-O
06	1026	1022	C-H bending modes of Alcohol
07	1125	1125	C-O Stretching vibration
08	1054/1056/1066	1057	Carboxylate group Bonded to Barium
09	1330	1331	C-H bending modes of Alcohol
10	1427	1423	COO- symmetric, asymmetric vibrations
11	1442	1398	O-H stretching
12	1570	1573	O-H bending mode of alcohol
13	1700	1702	Acetate Bonded to Barium
14	1744	1727	>C=0
15	1745/1743/1751	1750	BaCO ₃
16	2333/2343	2335	C=O Stretching Vibration
17	2835, 2823	2853	C-H bending of Alcohol
18	3010	3016	C-H stretching vibration, CH ₂ , CH ₃
19	3433,3430	3416	O-H stretching vibration of Water

Table 5.1 IR table of Barium Titanate Xerogel heat treated at different temperatures

FTIR analysis was carried out for the samples of batch1, batch 2, batch 3, batch 4 calcined at 400°C, 500°C and 700°C, the functionalized MWCNT, and 110°C dried xerogel sample of batch 1 for detection of the presence of functional groups. The functionalised MWCNT shows characteristic IR peaks at 1125cm⁻¹,1442 cm⁻¹, 1744 cm⁻¹, 2835 cm⁻¹, 2823 cm⁻¹, 3425 cm⁻¹ that corresponds to the C-O Stretching mode vibrations, O-H vibrations, >C=O vibrations, C-H bending vibrations, C-H, stretching vibrations and O-H vibrations respectively[54], [55],[56]. These characteristic peaks were found to be present for Batch 2 and Batch 4 samples. Which can be attributed to the presence of CNT but up to a temperature of 500°C. The associated CNT bands become diffused with increasing temperature from 400°C to 500°C due to loss of CNT. In figure 5.2, FTIR of the dried xerogel shows the characteristic absorption band at 3433 cm⁻¹ that can be assigned to the –OH stretching vibration of water [52] while another characteristic peak at 1567 cm⁻¹ is due to -OH bending mode of alcohol. The absorption band at 3016 cm⁻¹

is due to C-H stretching vibration and advocates the presence of CH_2 and CH_3 functional groups of the alkoxide[78]. Two other bands at 1700 cm–1 and 1427 cm–1 clearly indicate asymmetric and symmetric stretching vibrations of carboxylate groups which infer that acetate groups have bonded to barium atoms[79]. However, with increase in temperature the above characteristic absorption bands (3433cm-1, 1567 cm⁻¹, 3016 cm–1) ceases to exist due to progressive removal of the volatile compounds.

The presence of Ti-O-Ti and Ti-O bonds between 500cm^{-1} and 800cm^{-1} IR region are the molecular fingerprint of BaTiO₃. Figure 5.9 shows these characteristic bands become more prominent with an increase in temperature that can be ascribed to the formation of BaTiO₃ [52]. The disappearance of the band at 1700 cm^{-1} which corresponds to the Barium attached acetate groups also ascertains the above fact. The IR band(1745 cm⁻¹) corresponding to Barium carbonate also decreases sharply with increasing temperature but still persists up to 700°C. The intensity of this band is found to be highest for 500° C calcined samples. This suggests that the maximum rate of carbonation and maximum concentration of carbonates was at a temperature of around 500 °C.







Figure 5.3 FTIR Spectra of Batch 1 heat-treated at $400^{\circ}C$



Figure 5.4 FTIR Spectra of Batch 2 heat-treated at 400°C



Figure 5.5 FTIR Spectra of Batch 4 heat-treated at 400°C



Figure 5.6 FTIR Spectra of Batch 1 heat-treated at 500°C



Figure 5.7 FTIR Spectra of Batch 2 heat-treated at 500°C



Figure 5.8 FTIR Spectra of Batch 4 heat-treated at 500°C



Figure 5.9 FTIR Spectra of Batch 1 heat-treated at 700°C

5.2 Differential Thermal Analysis

Figure 5.10 & 5.11 shows the DTA study carried out on the samples of Batch 1 & Batch 3 (110°C calcined pure BaTiO₃ and 0.15 wt% CNT-BaTiO₃ Sample). The dried xerogels were subjected to thermal degradation from room temperature to 1000°C in the normal oxidizing atmosphere. The thermal analysis results can be categorized three major segments corresponding to - Dehydration, Pyrolysis, and Formation. Low-temperature endothermic peak around 142°C can be ascribed to the vaporization of residual or non-structural water and volatile organic solvents (Acetic Acid, Ethyl Alcohol in the sample) which is evident in both the samples' DTA and can also be justified from the FTIR analysis[52], the characteristic bands of Alcohol, Water in FTIR decrease with increase in temperature. The area under the curve of the endo peak in 100-200°C range of the CNT containing composite sample is larger as compared to the pure sample, which may be attributed to the presence of free surfactant SDS and unevaporated H₂O present in the composite[53]. The main decomposition of the precursor occurs in the temperature range of 200–500°C, in the DTA this corresponds to the endo peak at 355°C and proceeds via homogeneously distributed intermediate species, e.g., BaCO₃ and/or Ba, Ti oxycarbonate[38], the intermediate Barium Carbonate species have been identified in the FTIR analysis. The exothermic peaks 415°C in sample containing CNT occurs 10°C after the peak that occurs in pure sample of batch 1 at 425°C, this can be due to the presence of CNT, which prevents the decomposition of the residual barium carbonate at high temperatures[62-63]. The endothermic peak in the DTA at 620°C and 635°C of sample of batch 1 and batch 3 respectively are indications of the decomposition of intermediate carbonate phases. This can

also be verified from FTIR data of samples calcined at 500°C. The temperature range 430-1000°C corresponds to the formation of BaTiO₃ [60],[61].

The loss on ignition results of Batch 1 and Batch 3 heat-treated at 400°C, 500°C, and 700°C for 2 hours are as follows:

Temperature	Sample	LOI %
400°C	Batch 1 sample	26.934
	Batch 3 sample	26.424
500°C	Batch 1 sample	27.762
	Batch 3 sample	28.625
700°C	Batch 1 sample	36.381
	Batch 3 sample	36.448

Table 5.2 Loss on Ignition of Batch 1 & Batch 3 Xerogel

The LOI of Batch 1 & Batch 3 clearly indicate and verify that up to 400°C the CNT persisted in the composite sample, so the LOI of Batch 3 at 400°C is lesser as compared to Batch 1. But at higher temperature the LOI of batch 3 is more than LOI of batch 1 due to oxidation of CNT above 500°C. This also justifies the right shift of exothermic peaks for batch 3 as seen in DTA, where the CNTs present in the sample increased the oxidation resistance of the intermediate carbonates[56].

The differential thermal analysis can be summarised as the following [60],[61] :

- (i) De-hydration of the xerogel (xerogel100-200°C).
- (ii) Pyrolysis of the dehydrated xerogel (200-350°C).
- (iii) Formation of the intermediate phases (350-600°C).
- (iv) Formation of barium titanate and Crystallization (600-1000°C).



Figure 5.10: Differential Thermal Analysis of Batch 1 precursor



Figure 5.11: Differential Thermal Analysis of Batch 3 precursor

5.3 Phase Analysis by X-ray Diffraction

The –COOH functionalized MWCNT used in the Barium Titanate-CNT composite preparation was characterized using Xray diffraction (figure 5.12). The scanning was done between 10 to 80° (2 Θ). The data revealed the presence of two characteristic peaks at 25.70° and 42.43° corresponds to (002) and (100) planes of the carbon atoms respectively[53]. The Xrd plot of the samples calcined at 400°C of batch 2, batch 3and batch 4 is highly amorphous in nature, we get diffused and overlapped peaks, after smoothening, we get an idea of the probable peaks, among which non-stochiometric Oxides of Titanium and Barium are present. The LOI of CNT tells that CNT remains intact till 400°C. The XRD of sample batch 2 & batch 4 shows the presence of CNT peaks. The pure precursor sample of Barium Titanate derived by sol-gel lacks any CNT peaks at 25.70° and 42.43°. So, it can be confirmed along with FTIR and XRD the presence of CNT up to 400°C temperature.

Figure 5.16, Figure 5.17, Figure 5.18 and Figure 5.19 are the Xrd of samples of Batch 1, Batch 2, Batch 3, and Batch 4 calcined at temperature 500°C. Even at this temperature the peaks are a bit diffused and some peaks superimpose onto each other, this shows the lack of crystallinity at 500°C. The observation from 500°C samples is that formation of TiO₂ and BaCO₃. Barium carbonate has a prominent peak intensity among the other intermediates present in the samples at 500°. Second observation which can be concluded that the presence of CNT peaks at 25.70° and 42.43°. The pure sample of Batch 1 lacks CNT peaks, but these peaks are present in

samples batch 2, batch 3 & batch 4. The CNT peaks are of less intensity than the peaks at 400°C samples. But the amorphous nature has slightly decreased from 400°C samples' XRDs.

The Xrd of sample of Batch 4 calcined at 700°C (figure 5.20), shows well-defined peaks at 2 Θ angles 22.192°, 31.579°, 56.219°, and 79.168° which corresponds to the JCPDS data of 05-0626 [52] and confirm the formation of high purity and Tetragonal phase barium titanate. The XRD pattern is well crystallized at 700°C. But there were some peaks corresponding to nonstoichiometric Barium Titanate, Ba_{0.992}TiO₃ at 2 Θ 38.90°, 45.314°, 70.439°. The XRD pattern in Figure 6.21 shows that BaTiO3 is well-crystallized in the sample calcined at 700 °C for 2 h. The CNT peaks are not present at 700°C calcined sample, which is being confirmed from XRD.The CNT peaks, that were there in the 400°C and 500°C calcined CNT containing samples are absent in 700°C calcined CNT containg sample.



Figure 5.12 X-ray diffraction pattern of Functionalised Multiwalled CNT



46 | Page







Figure 5.14 X-ray diffraction pattern of Batch 4 heat-treated at 400°C

Figure 5.15 X-ray diffraction pattern of Batch 1 heat-treated at 400°C















Figure 5.19 X-ray diffraction pattern of Batch 4 heat-treated at 500°C



Figure 5.20 X-ray diffraction pattern of Batch 4 heat-treated at 700°C

5.4 Surface Morphology study

Surface morphology of Batch 4 calcined at 500°C and 700°C is analyzed using SEM (Scanning Electron Microscopy). Typical SEM images reveal the aggregated and agglomerated structure of the composite. The presence of CNTs in the composite otherwise confirmed from the XRD analysis, FTIR spectra and Raman spectra is not distinguishable by SEM images. This may be either because of the Barium titanate has coated CNTs or the SEM resolution is too low to distinctly identify CNTs in nanometric range.



Figure 5.21: SEM photograph of Batch 3 heat-treated at 500°C



Figure 5.22: SEM photograph of Batch 3 heat-treated at 700°C

5.5 Raman Spectroscopy study

The Raman measurements were carried out on the samples calcined at 500°C and 700°C. It is evident from the Raman spectra of 500°C calcined sample, that CNT is present in the composite. The presence of CNT was evident from XRD and FTIR analysis as well. However, the characteristic peaks of Barium Titanate are diffused and of very low Intensity at 500°C. The two characteristic peaks of the functionalized CNT were observed at a Raman shift of 1338 cm⁻¹ and 1582 cm⁻¹. The intensity corresponding to these Raman shift is 4848.5 and 5287 respectively. Figure 5.23 shows the Raman spectra of pristine functionalized MWCNT, that was used in our work. The G band and D band of the pristine CNT are at Raman shift of 1343 cm⁻¹ and 1579 cm⁻¹. Close to the Raman shift of the CNT present in the composite Raman spectra. The most noteworthy point here is, the Ip/Ig value of the CNT in our composite is 0.92 which is much less form the Ip/Ig value of the pristine CNT 0.992, this corresponds to chemical bonding between the CNT and the host matrix. The decreasing of Ip/Ig refers to an increase in stability of the Carbon nanotube in the matrix at that temperature with respect to the pristine CNT. This decrease may also be due to the coating of the CNT by the matrix.

Figure 5.25 and 5.26 shows the stretching mode of Ti-O at around 160, 266, 306, 523, 717 cm⁻¹. From table 5.3 it can be observed that the observed Raman shifts are close to the shifts mentioned in literature [60], [80]. There is no significant change in the observed Raman

spectra. The peak at 306 cm⁻¹ is the characteristic of tetragonal phase of BaTiO3. This also supports the observation of the XRD sample of batch 4. The presence of tetragonal phase is found to be around 305 cm⁻¹. The characteristic peaks of CNT that we got in 500°C calcined sample are not present in the Raman spectra of batch 4.

Observed Raman Spectrum (cm ⁻¹)	Raman Spectrum fromLiterature [60], [81](cm ⁻¹)	Remarks
266, 262	269	Barium Titanate
306, 305	306	Barium Titanate
523, 528	516	Barium Titanate
717, 717	720	Barium Titanate
1342, 1338	1340	D band of CNT
1584, 1582	1580	G band of CNT

Table 5.3 Comparison of Raman shift as observed and in literature



Figure 5.23: Raman Spectra of pristine CNT



Figure 5.24: Raman Spectra of sample Barium Titanate with 0.3 wt% CNT calcined at 500°C







Figure 5.26: Raman Spectra of Batch 4 heat-treated at 700°C

5.6 UV-VIS spectroscopy analysis

UV-Visible spectroscopy analysis of Batch 1, Batch 2, Batch 3 and Batch 4 calcined at 400°C was performed to understand the reflectance characteristics of the materials that depend on a number of factors, and one such factor is band gap. Diffuse reflectance was developed to facilitate analysis of materials such as papers and powders in their neat state. The common characteristic of these materials is their internal inhomogeneities. The propagation of light through such inhomogeneous media differs significantly from the homogeneous material since the light scatters off points in its path. The expression proposed by Kubelka-Munk was used

for bandgap estimation of our calcined powder samples from the reflectance spectra. UV-Vis study reveals that, the band gap of composite increases as a function of CNT wt %. The Bandgap data obtained from the samples calcined at 400°C, is not absolute as the samples are mostly amorphous in nature at this temperature range. But it gives an indication of the trend that with an increment in CNT wt% the bandgap increases; thus superior dielectric properties of this composite may be envisaged.



Figure 5.27: Kubelka-Munk plot of Batch 1 heat-treated at 400°C



Figure 5.28: Kubelka-Munk plot of Batch 2 heat-treated at 400°C







Figure 5.30 Kubelka-Munk plot of Batch 4 sample heat-treated at $400^{\circ}C$

The band gap measurements that we got from Kubelka-Munk analysis is as follows:



Table 5.4: Bandgap as a function of CNT wt%

CNT wt%	Bandgap(eV)
0	1.91
0.05	1.94
0.15	2.17
0.30	2.36

Chapter 6

CONCLUSION

..........

111111

.

The synthesis and characterization of CNT dispersed Barium Titanate composite has been elaborately studied here to unveil the potentials of this composite. From the present investigation, the following conclusion may be drawn as

- Homogeneously distributed CNT dispersed Barium Titanate sol was synthesized successfully through sol-gel technique where the dispersion of CNT was stable up to gelation.
- XRD and Raman analysis support the formation of Tetragonal BaTiO₃ (Barium Titanate) through transformation of intermediate phases on calcination of dried gel at 700°C. The presence of CNT within the Barium Titanate matrix is found well in amount up to 500°C as confirmed from XRD, FT-IR, Raman spectroscopy analysis.
- Raman spectral analysis showed that the relative intensity ratio (**R**=**I**_D/**I**_G) of the homogeneously distributed CNT within Barium Titanate matrix decreases as compared to the Pristine CNT. A larger value of **I**_D/**I**_G is associated with higher disorders of the carbon, thus we can infer that the CNT became more stable and ordered when dispersed homogeneously within the Barium titanate matrix. This may be ascribed to coating of the CNT by barium titanate.
- UV-Visible spectroscopy analysis of the calcined sample(400°C) conveys that the bandgap of the calcined sample increases as a function of weight % of CNT content. This indication serves as a guiding light for the preparation of high-performance dielectric materials by utilizing the excellent dielectric properties of Barium Titanate CNT composite.

Scope for Further Research

It would be very interesting to investigate the properties of the synthesized samples which are yet to be explored. Further research will yield more integrated result on this topic which will assist us to exploit this material in several industrial and scientific arenas. So there is always a scope to improve the performance and process. More additional investigations that we could perform are as follows:

- Electrical properties of these composites could also be very interesting to note.
- Investigation of sintering properties of the composite material synthesized.
- Synthesis of these composite materials from different processing routes (Solid state, Hydrothermal) must be carried out and a comparative study must be done to optimize the best route that can be commercially exploited.

REFERENCES

References

[1] Cernea, M. "Methods for preparation of BaTiO3 thin films." Journal of Opotoelectronics and Advanced Materials Vol 6.4 (2004): 1349-1356.

[2] Phule, P. P., and S. H. Risbud. "Sol-gel synthesis of barium titanate powders using barium acetate and titanium (IV) isopropoxide." Advanced Ceramic Materials;(USA) 3.2 (1988).

[3] Kamalasanan, M. N., N. Deepak Kumar, and Subhas Chandra. "Structural and microstructural evolution of barium titanate thin films deposited by the sol-gel process." Journal of applied physics 76.8 (1994): 4603-4609.

[4] Mazdiyasni, 1. _K S., R. T. Dolloff, and J. S. Smith. "Preparation of High-Purity Submicron Barium Titanate Powders." Journal of the american Ceramic Society 52.10 (1969): 523-526.

[5] Mazdiyasni, K. S. "Fine particle perovskite processing." American Ceramic Society Bulletin 63.4 (1984): 591-594.

[6] Flaschen, Steward S. "An aqueous synthesis of barium titanate." Journal of the American Chemical Society 77.23 (1955): 6194-6194.

[7] D. W. Richerson, Modern ceramic engineering: Properties, processing, and use in design Second Edition, Marcel Dekker, Inc, 1992.

[8] Rahman, M. K., et al. "Effect of Sintering Time on Dielectric Properties of Barium Titanate and Nb Doped Barium Titanate." Applied Mechanics and Materials. Vol. 860. Trans Tech Publications, 2017.

[9] Ritter, J. J., R. S. Roth, and J. E. Blendell. "Alkoxide Precursor Synthesis and Characterization of Phases in the Barium-Titanium Oxide System." Journal of the American Ceramic Society 69.2 (1986): 155-162.

[10] Phule, Pradeep P., Srini Raghavan, and Subhash H. Risbud. "Comparison of Ba (OH) 2, BaO, and Ba as starting materials for the synthesis of barium titanate by the alkoxide method." Journal of the American Ceramic Society 70.5 (1987): C-108.

[11] Harrop, P. J., and D. S. Campbell. "Selection of thin film capacitor dielectrics." Thin Solid Films 2.4 (1968): 273-292.

[12] Wooten, F. T. "A proposed ultra-sensitive miniature temperature sensor." Proceedings of the IEEE 55.4 (1967): 564-564.

[13] R. S. Muller, J. Conragan, IEEE Trans. Electron. Devices ED-12, 590 (1965).

[14] J. R. Fiebiger, R. S. Muller, J. Appl. Phys. 38, 1948 (1967).

[15] A. B. Kaufman, IEEE Trans. Electron. Devices ED-16, 562 (1969).

[16] Borrelli, N. F., and M. M. Layton. "Electrooptic properties of transparent ferroelectric glass—Ceramic systems." IEEE Transactions on Electron Devices 16.6 (1969): 511-514.

[17] G. W. Taylor, IEEE Trans. Electron. Devices ED-16, 565 (1969).

[18] Performance of barium titanate@carbon nanotube nanocomposite as an electromagnetic wave absorber by Gan Jet Hong Melvin, Qing-Qing Ni, Zhipeng Wang First published: 24 October 2016, doi.org/10.1002/pssa.201600541

[19] Rao, B. G., Mukherjee, D., & Reddy, B. M. (2017). Novel approaches for the preparation of nanoparticles. Nanostructures for Novel Therapy, 1–36. doi:10.1016/b978-0-323-46142-9.00001-3

[20] Sahu, Jyoti Prakash. Preparation and Characterization of Carbon Nanotubes Barium Titanate Composites. Diss. 2013.

[21] Suzuki, Keigo; Kijima, Kazunori (2005). "Optical Band Gap of Barium Titanate Nanoparticles Prepared by RF-plasma Chemical Vapor Deposition". Jpn. J. Appl. Phys. 44(4A): 2081–2082. Bibcode:2005JaJAP..44.2081S. doi:10.1143/JJAP.44.2081

[22] Barium titanate & changes, www.doitpoms.ac.uk/tlplib/ferroelectrics/phase_changes.php

[23] Janas, Dawid (2018). "Towards monochiral carbon nanotubes: a review of progress in the sorting of single-walled carbon nanotubes". Materials Chemistry Frontiers. 2 (1): 36–63. doi:10.1039/C7QM00427C. ISSN 2052-1537.

[24] S. B. Sinnott & R. Andreys (2001). "Carbon Nanotubes: Synthesis, Properties, and Applications". Critical Reviews in Solid State and Materials Sciences. 26 (3): 145–249. Bibcode:2001CRSSM..26..145S. doi:10.1080/20014091104189.

[25] Pavlovic, V. P., et al. "Synthesis of BaTiO 3 from a Mechanically Activated BaCO 3-TiO 2 System." Science of Sintering 40.1 (2008).

[26] Mayank Rai and Sankar Sarkar (July 27th 2011). Carbon Nanotube as a VLSI Interconnect, Electronic Properties of Carbon Nanotubes, Jose Mauricio Marulanda,

IntechOpen,DOI:10.5772/17679.Availablefrom:https://www.intechopen.com/books/electroni c-properties-of-carbon-nanotubes/carbon-nanotube-as-a-vlsi-interconnect

[27] Wang, Jun, Yu Chen, and Werner J. Blau. "Carbon nanotubes and nanotube composites for nonlinear optical devices." Journal of Materials Chemistry 19.40 (2009): 7425-7443.

[28] H. M. Rosenberg, "The solid state", Third Edition, Oxford University press Inc., (1988)

[29] R. M. Rose, L. A. Shepard, and J. Wulff, "The structure and properties of materials", Wiley Eastern private limited, (1971).

[30] M. Allison, "Metrology and analysis of nano-particulate barium titanate dielectric material", MSc Thesis, Kansas university, Manhattan, Kansas, 2007.

[31] Osman, KOLTHOUM ISMAIL. "Synthesis and characterization of BaTiO 3 ferroelectric material." (2011).

[32] D. Segal, "Chemical synthesis of advanced ceramic materials", Cambridge University Press, (1991).

[33] Buzea, Cristina; Pacheco, Ivan; Robbie, Kevin (2007) "Nanomaterials and nanoparticles:
Sources and Toxicity". Biointerphases. 2 (4):MR17MR71. arXiv:0801.3280.
doi:10.1116/1.2815690. PMID 20419892

[34] A. J. Dekker, "Solid State Physics", The Macmillan press LTD., 1958.

[35] Lufaso, Michael Wayne. Perovskite synthesis and analysis using structure prediction diagnostic software. Diss. The Ohio State University, 2002.

[36] Schwartz, Robert W. "Chemical solution deposition of perovskite thin films." Chemistry of materials 9.11 (1997): 2325-2340.

[37] Jana L., Petra S. and Trojan M. Study of perovskite compounds. Journal of Thermal Analysis and Calorimetry. 2008, 93 (3): 823 – 827.

[38] Kareiva A., Tautkus S., Rapalaviciute R., Jørgensen J.-E. and Lundtoft B. Sol-gel synthesis and characterization of barium titanate powders. Journal of Materials Science. 1999, 34: 4853-4857.

[39] Nahum M., Beltrán H., Cordoncillo E., Sinclair D. C., West A. R. Polymorphism and

dielectric properties of Nb-Doped BaTiO3. Journal of American Ceramic Society. 2008, 91 (1): 144-150.

[40] Masó N., Beltrán H., Cordoncillo E., Sinclair D. C. and West A. R. Polymorphism and dielectric properties of Nb-doped BaTiO3. Journal of American Ceramic Society. 2008, 91(1): 144-150.

[41] Gaikwad S. P., Dhage S. R., Potdar H. S., Samuel V. and Ravi V. Co-precipitation method for the proparation of nanocrystalline ferroelectric SrBi2Nb2O9 ceramics. Journal of Electroceramics. 2005, 14: 83-87.

[42] Vijatovi) M. M., Bobi) J. D. and Stojanovi) B. D., History and challenges of barium titanate: part II. Science of Sintering. 2008, 40: 235-244.

[43] Pavlovi) V. P., Pavlovic A. V. B., stojanovic B. D., Sreckovic T., Marinkovic B., Ristic

M. M.. The influence of heating rate ion sintering process of BaTiO3 ceramics. In:

Advanced science and technology of sintering. (Stojanovi) B. D., Skorokhod V. V. and

Nikoli), Eds.), Springer science + Business Media New York, 1999.

[44] Aga, Zubeda Bi H. "Synthesis and Characterization of Nano Sized Pure and Doped Barium Titanate Powders Prepared by Sol Gel Emulsion Technique." (2014).

[45] T. Ahmed, "Nanostructured barium titanate prepared through a modified reverse micellar route: Structural distortion and dielectric properties", J. Mater. Res., 20 [6] (2005) 1415-1421.

[46] Javey, Ali, and Jing Kong, eds. *Carbon nanotube electronics*. Springer Science & Business Media, 2009.

[47] Jiao, Liying, et al. "Narrow graphene nanoribbons from carbon nanotubes." *Nature* 458.7240 (2009): 877.

[48] Kashiwagi, Takashi, et al. "Flammability properties of polymer nanocomposites with single-walled carbon nanotubes: effects of nanotube dispersion and concentration." *Polymer* 46.2 (2005): 471-481.

[49] Shih, Wei-Yan, Arthur Wilson, and Willmar Subido. "Bonding pads for integrated circuits having copper interconnect metallization." U.S. Patent No. 6,329,722. 11 Dec. 2001.

[50] Shah, Badal, Todd Lafleur, and Aicheng Chen. "Carbon nanotube based electrochemical sensor for the sensitive detection of valacyclovir." *Faraday discussions* 164 (2013): 135-146.
[51] Endo, M., et al. "Vapor-grown carbon fibers (VGCFs): basic properties and their battery applications." *Carbon* 39.9 (2001): 1287-1297.

[52] Ashiri, R. "Detailed FT-IR spectroscopy characterization and thermal analysis of synthesis of barium titanate nanoscale particles through a newly developed process." Vibrational Spectroscopy 66 (2013): 24-29.

[53] Pisal, S. H., et al. "Functionalized multi-walled carbon nanotubes for nitrogen sensor." IOSR J. Appl. Chem 7 (2014): 49-52.

[54] Singh, Bhanu Pratap, et al. "Solvent free, efficient, industrially viable, fast dispersion process based amine modified MWCNT reinforced epoxy composites of superior mechanical properties." Adv Mater Lett 6.2 (2015): 104-113.

[55] do Amaral Montanheiro, Thaís Larissa, et al. "Effect of MWCNT functionalization on thermal and electrical properties of PHBV/MWCNT nanocomposites." Journal of Materials Research 30.1 (2015): 55-65.

[56] Sriram, J. G., et al. "Characteristics of BaTiO3–carbon nanotube composite synthesised by mechanical milling." Materials Research Innovations 19.4 (2015): 265-269.

[57] Fan, Benhui. Dielectric properties of carbon nanotube-BaTiO₃ hybrids reinforced PVDF composites. Diss. Université Paris-Saclay, 2015.

[58] Huang, Qing, et al. "Sintering and thermal properties of multiwalled carbon nanotube– BaTiO 3 composites." Journal of Materials Chemistry 15.20 (2005): 1995-2001.

[59] Yu, Lujun, et al. "Nanostructured Barium Titanate/Carbon Nanotubes Incorporated Polyaniline as Synergistic Electromagnetic Wave Absorbers." *Journal of Nanomaterials*2016 (2016).

[60] Thandar, Win, Naing Kyaw, and Mar Tun Khin. "Synthesis of Barium Titanate from Titanyl Acylate Precursor by Sol-precipitate Method." (2008).

[61] Formation Mechanism of Barium Titanate by Solid-State Reactions, International Journal of Scientific & Engineering Research, Volume 5, Issue 7, July-2014 ISSN 2229-5518. Kolthoum I. Othman1, Ahmed A. Hassan1, Omar A. A. Abdelal1, Ezzat S. Elshazly1, M. El-Sayed Ali1, S. M. El-Raghy2, S. El-Houte1.

[62] S. Ohara, A. Kondo, H. Shimoda, K. Sato, H. Abe and M. Naito: 'Rapid mechanochemical synthesis of fine barium titanate nanoparticles', Mater. Lett., 2008, 62, 2957–2959.

[63]. D. Hennings and S. Schreinemacher: 'Characterization of hydrothermal barium titanate', J. Eur. Ceram. Soc., 1992, 9, 41–46.

[64] Y. Qing, Y. Mu, Y. Zhou, F. Luo, D. Zhu, and W. Zhou, "Multiwalled carbon nanotubes-BaTiO3/silica composites with high complex permittivity and improved electromagnetic interference shielding at elevated temperature," Journal of the European Ceramic Society, vol. 34, no. 10, pp. 2229–2237, 2014.

[65] Z. Zheng, B. Xu, L.Huang, L.He, and X.Ni, "Novel composite of Co/carbon nanotubes: synthesis, magnetism and microwave absorption properties," Solid State Sciences, vol. 10, no. 3, pp. 316–320, 2008.

[66] H. F. Li, J. Wang, Y. H. Huang et al., "Microwave absorption properties of carbon nanotubes and tetrapod-shaped ZnO nanostructures," Materials Science and Engineering B, vol. 175, no. 1, pp. 81–85, 2010.

[67] Z. Guo, S.-E. Lee, H. Kim et al., "Fabrication, characterization and microwave properties of polyurethane nanocomposites reinforced with iron oxide and barium titanate nanoparticles,"

Acta Materialia, vol. 57, no. 1, pp. 267–277, 2009.

[68] X. Huang, Z. R. Chen, L. F. Tong, M. N. Feng, Z. J. Pu, and X. B. Liu, "Preparation and microwave absorption properties of BaTiO3@MWCNTs core/shell heterostructure," Materials Letters, vol. 111, pp. 24–27, 2013.

[69] Y.-F. Zhu, Q.-Q. Ni, and Y.-Q. Fu, "One-dimensional barium titanate coatedmulti-walled carbon nanotube heterostructures: synthesis and electromagnetic absorption properties," RSC

Advances, vol. 5, no. 5, pp. 3748–3756, 2015.

[70] Feng Y, Qiu T, Shen C. Journal of Magnetism and Magnetic Materials 2007;318:8–13.

[71] Mu G, Shen H, Qiu J, Gu M. Applied Surface Science 2006;253:2278-81.

[72] Wei J, Yang X, Zhan Y, Meng F, Zhao R, Zhong J, et al. Materials Letters 2012;67:135-8

[73] Ma Z, Zhao R, Yang X, Wei J, Meng F, Liu X. Materials Letters 2012;69:30-3

[74] Carbon Nanotubes Characterization by X-ray Powder Diffraction – A Review in Current Nano Science, february 2015, by Rasel Dasa, Sharifah Bee Abd Hamida, Md. Eaqub Alia, Seeram Ramakrishnab, and Wu Yongzhib [75] Kareiva, A., et al. "Sol-gel synthesis and characterization of barium titanate powders." Journal of materials science 34.19 (1999): 4853-4857.

[76] S. Sanna, 1. C. (2011). Barium titanate ground- and excited-state properties from first-principles calculations. American Physical Society, 054–112.

[77] Razak, Nurul Athirah Abd, Noriza Ahmad Zabidi, and Ahmad Nazrul Rosli. "A first principle study of band structure of tetragonal barium titanate." AIP Conference Proceedings. Vol. 1875. No. 1. AIP Publishing, 2017.

[78] M. Burgos, M. Langlet, Thin Solid Films 349 (1999) 19–23.

[79] S. Tangwiwat, S.J. Milne, J. Non-Cryst. Solids 351 (2005) 976–980.

[80] Lazarevica, Z., et al. "Characterization of barium titanate ceramic powders by Raman spectroscopy." Proceedings of the Tenth Annual Conference of the Materials Research Society of Serbia. 2008.

[81] Dresselhaus, Mildred S., et al. "Raman spectroscopy of carbon nanotubes." Physics reports 409.2 (2005): 47-99.