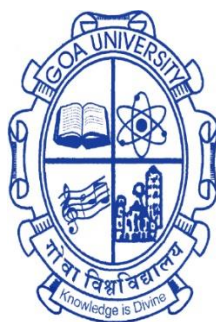


**OVERVIEW ON SYNTHESIS,
CHARACTERIZATION
AND APPLICATION
OF BaTiO₃**

An MSc Dissertation report by :

NITESH S. NAIK



SCHOOL OF CHEMICAL SCIENCES

GOA UNIVERSITY

GOA 403206

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By
Mast. Nitesh S. Naik

To the

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Goa University
Goa 403206
APRIL 2022

CERTIFICATE

This is to certify that the dissertation entitled “ ***Overview on synthesis, characterization and application of BaTiO₃***” is bonafide work carried out by Mast. Nitesh S. Naik under my supervision in partial fulfilment of the requirement for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

Prof. Dr. Vidyadatta Verenkar
Dean, School of Chemical Sciences
Goa University

Dr. Shrikant Naik
Guiding teacher

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1. INTRODUCTION:

BaTiO₃ is a synthetic perovskite that crystalizes itself in ideal perovskite structure or in hexagonal modification. Goldschmidt firstly studied and prepared synthetic perovskites on varying composition together with Barium titanate¹. Barium titanate (BaTiO₃) has been of practical interest for more than 60 years because of its attractive properties. 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 samples². It has the appearance of a white powder or transparent crystals. It is insoluble in water and soluble in concentrated sulfuric acid³.

Barium titanate (BaTiO₃) is a very attractive material in the field of electroceramics and microelectronics due to its good characteristics. Its high dielectric constant and low loss characteristics make barium titanate an excellent choice for many applications, such as capacitors, multilayer capacitors (MLCs) and energy storage devices. Doped barium titanate has found wide application in semiconductors, positive temperature coefficient resistors, ultrasonic transducers, piezoelectric devices, and has become one of the most important ferroelectric ceramics⁴.

2. STRUCTURE OF BARIUM TITANATE:

The perovskite-like structure, named after the CaTiO₃ perovskite mineral, is a ternary compound of formula ABO₃ that A and B cations differ in size. Perovskite is first discovered by Russian mineralogist Gustave Rose from Ural mountain in Russia. It was named after Russian mineralogist Lev Perovski¹.

It is considered an FCC derivative structure in which the larger A cation and oxygen together form an FCC lattice while the smaller B cation occupies the octahedral interstitial sites in the FCC array. The structure is a network of corner-linked oxygen octahedra, with the smaller cation filling the octahedral holes and the large cation filling the dodecahedral holes.

In the BaTiO₃ crystal structure, the Ti atoms are coordinated with six O atoms to form octahedral clusters [TiO₆], whereas the Ba atoms are coordinated with twelve O atoms to produce [BaO₁₂] clusters⁵. In the FCC lattice the A-larger cation in the corner, the B-smaller cation in the middle of the cube, and the anion, commonly oxygen, in the centre of the face edges, where A is a monovalent, divalent or trivalent metal and B a pentavalent, tetravalent or trivalent element, respectively. The coordination number of A (Ba²⁺ Barium) is 12, while the coordination number of B (Ti⁴⁺ Titanium) is 6³. Also, it is unnecessary that the anion is oxygen. For example, fluoride, chloride, carbide, nitride, hydride and sulfide perovskites are also classified as the perovskite structures. As a result, we can say that perovskite structure has a wide range of substitution of cations A and B, as well as the anions, but remember that the

principles of substitution must maintain charge balance and keep sizes within the range for particular coordination number. Because the variation of ionic size and small displacements of atoms that lead to the distortion of the structure and the reduction of symmetry have profound effects on physical properties, perovskite structure materials play such an important role in dielectric ceramic.

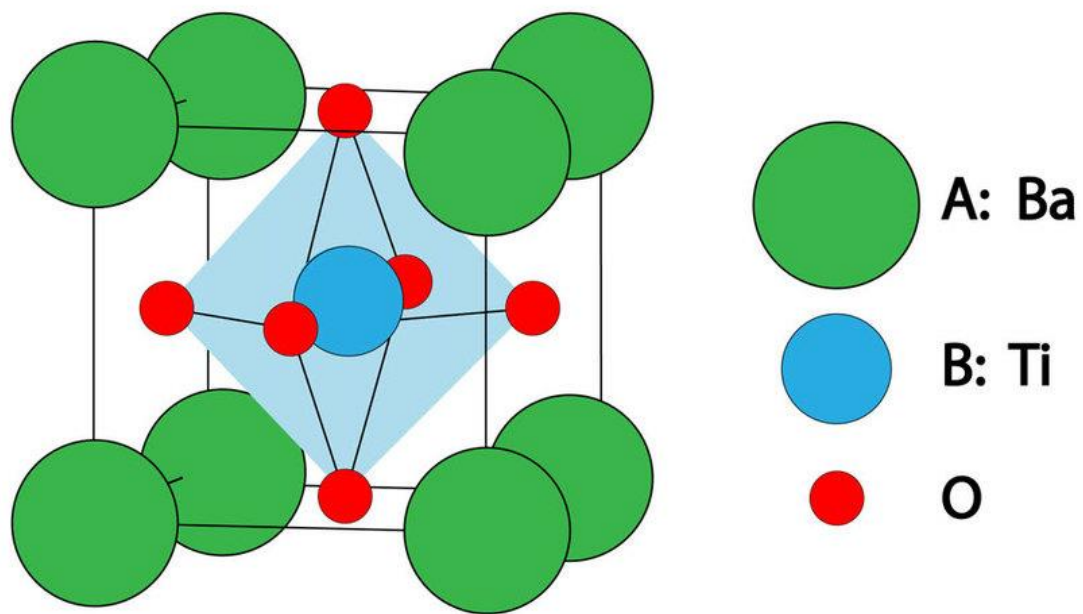


Figure.1. Barium titanate structure

3. PHASE TRANSITION IN BARIUM TITANATE:

Barium titanate exists in five different polymorphic crystalline forms; there are three (tetragonal, orthorhombic, and rhombohedral) which are ferroelectric, and two paraelectric (cubic as well as hexagonal). The tetragonal polymorph is the most widely used because of its excellent ferroelectric, piezoelectric, and thermoelectric properties. The Curie point T_c of barium titanate is 120°C . Above 120°C the original cubic cell is stable up to 1460°C . Above this temperature a hexagonal structure is stable. When the temperature is below the Curie point, crystallographic changes in BaTiO_3 occur, first at about 120°C a ferroelectric transition between the cubic, paraelectric and ferroelectric phase of tetragonal structure takes place. At 5°C , the transition to a phase of the orthorhombic structure goes on and at -90°C to the low temperature phase having a trigonal structure.

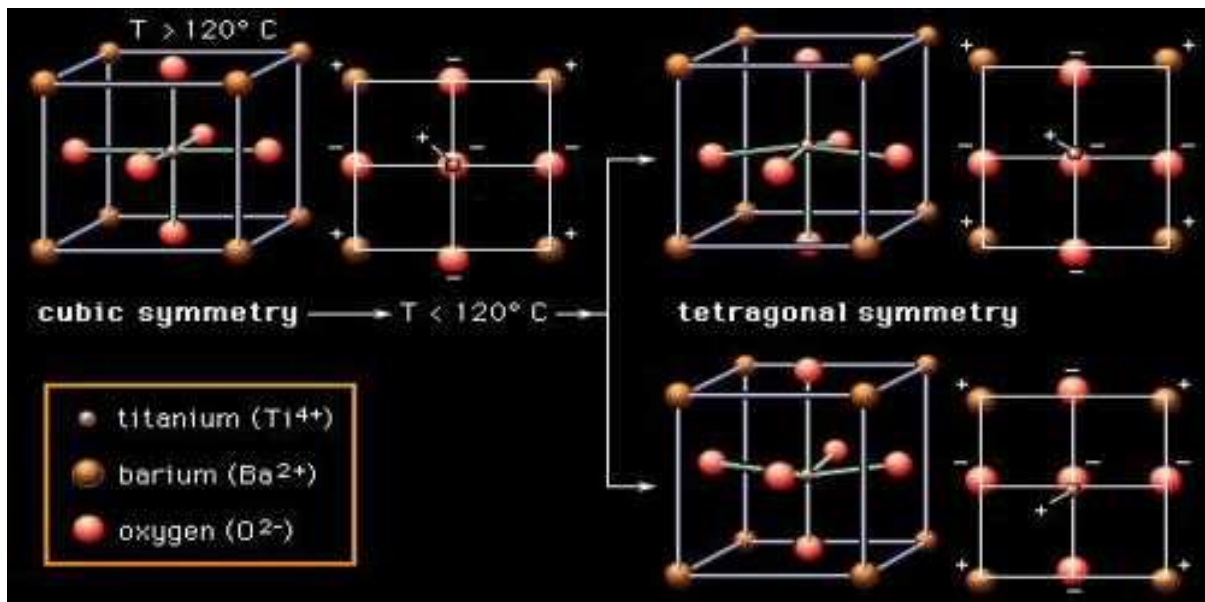


Figure.2. Phase transition at curie temperature.

At the Curie point Ti -ions are all in equilibrium positions in the center of their octahedra, but with a decrease of the temperature, Ti -ions jumps between energetically favorable positions out the of octahedron center. These changes can be related to structural distortion, lengthening of the bonds or their shortening, so crystallographic dimensions of the barium titanate lattice change with temperature².

4. PROPERTIES OF BARIUM TITANATE:

The properties of BaTiO_3 have been the subject of study of many authors. It is well known that the properties of BaTiO_3 powders and ceramics strongly depend on the synthesis route and sintering regime. Barium titanate is the first known ferroelectric ceramics and a good candidate for a variety of applications due to its excellent dielectric, ferroelectric and piezoelectric properties.

4.1. Ferroelectric property

Ferroelectricity is a phenomena discovered in 1921, it is analogous to the ferromagnetic phenomena of iron. Ferroelectric materials are the materials that y retain a dipole even after an applied voltage has been removed and exhibit spontaneous polarization. Ferroelectric behavior is dependent on the crystal structure. The crystal must be noncentric and contain alternate atom positions or molecular orientations to permit the reversal of dipole and the retention of polarization after the voltage is removed. Ferroelectric ceramics do not absorb moisture, nor do they dissolve in water, being able to perform over a wide range of operating temperatures. However, every ferroelectric has a temperature point above which the material becomes substantially non-electric, i.e. dielectric, known as its Curie temperature. 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 result⁶.

Amongst other ferroelectric materials, barium titanate (BaTiO_3) is a useful and technologically important material owing to its ferroelectric behavior at and above room temperature, and having polarization (P_s) values several orders higher than the potassium dihydrogen phosphate-type ferroelectrics³.

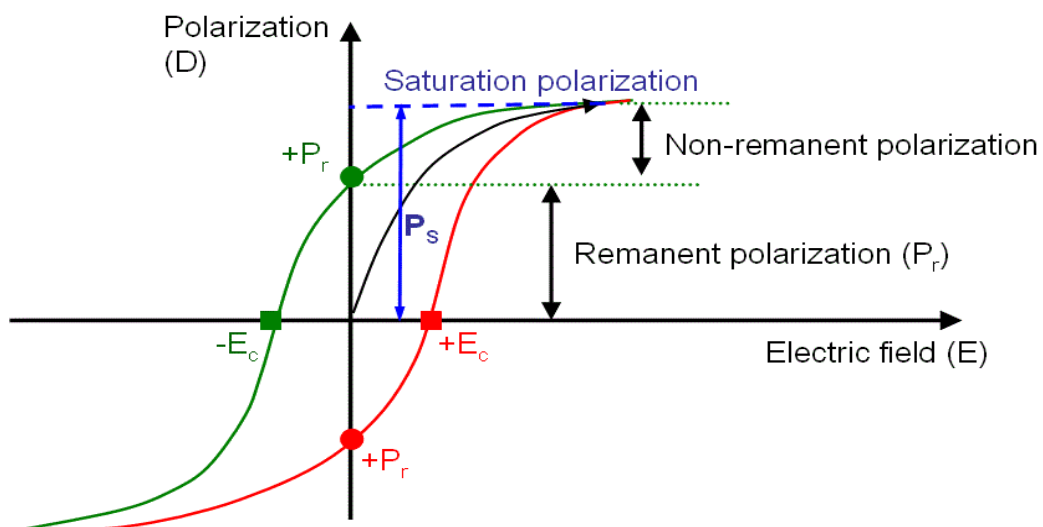


Figure.3. Hysteresis loop of barium titanate

4.2. Dielectric property

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. All the crystal phases of barium titanate are good dielectrics. The reason that the barium titanate is such a good dielectric is that the dielectric constant depends on the amount of polarization that the electric field brings about. Due to the fact that barium titanate can be extremely polarized in an electric field the dielectric constant is also similarly high.

BaTiO₃ was the first material used for manufacturing dielectric ceramics capacitors, multilayer capacitors etc. It is used for this application due to its high dielectric constant and low dielectric loss. The values of the dielectric constant depend on the synthesis route, which means purity, density, grain size etc. The dielectric constant is also dependent on temperature, frequency and dopants⁴. The temperature dependence of the dielectric constant was reported on in a number of papers, where barium titanate was prepared by different types of synthesis.

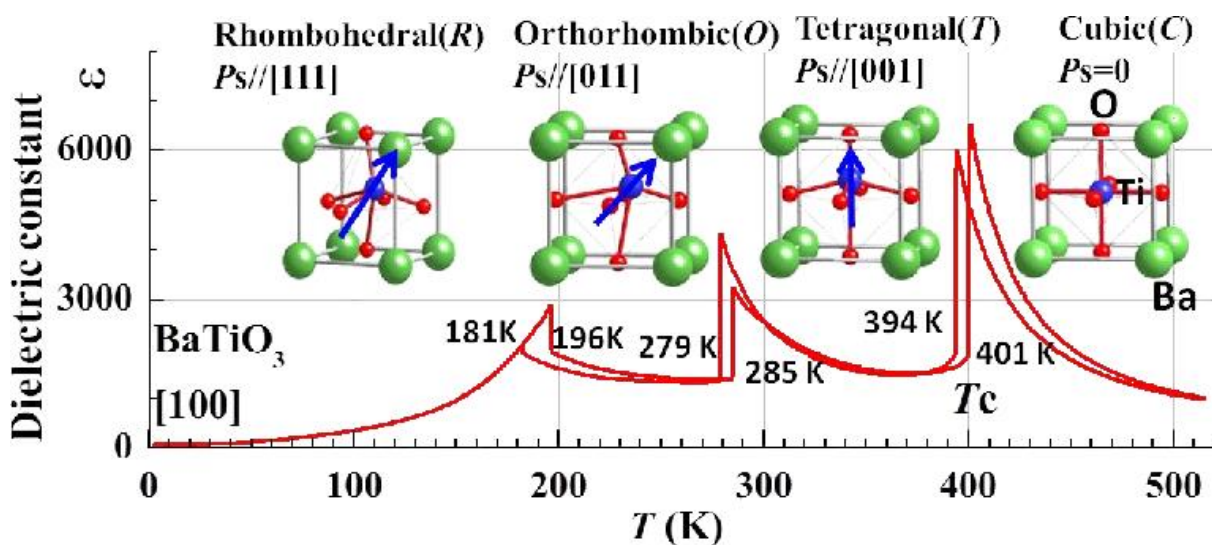


Figure.4. Dependence of dielectric constant of BaTiO₃ on temperature

4.3. Piezoelectric property

Barium titanate is most widely used for its strong piezoelectric characteristics. The word “piezoelectricity” is derived from the Greek “piezein”, which means to squeeze or press, hence, piezoelectricity is the generation of electricity as a result of mechanical pressure. A necessary condition for piezoelectricity to exist is noncentrosymmetry in the crystal. Two effects are operative in piezoelectric crystals, in general, and in ferroelectric ceramics, in particular.

Due to excellent piezoelectric properties (polarization occurs after applying pressure), BaTiO₃ is used in developments of counters, data collectors, sound detectors, as well as in microelectronic devices fabrication⁷.

5. LITERATURE REVIEW:

5.1. Methods of preparation

BaTiO₃ synthesis techniques were mentioned in a lot of papers. The selected method for barium titanate synthesis depends on cost, but even more important is the end application. The quality of the powders is not only influenced by the synthesis route but also by the starting materials used. As miniaturization of electronic devices continues to demand smaller particle size powders with controlled morphology, the desired characteristics of the starting powder become a critical issue. The successful synthesis of barium titanate powder with their unique dielectric properties largely depends on the purity and crystal structure that greatly influences final properties.

➤ Conventional solid-state reaction

Traditionally, barium titanate is prepared by a solid-state reaction that involves ball milling or grinding of BaCO₃ or BaO and TiO₂. The mixture has to be calcined at high temperature. In some reports the needed calcination temperature was as high as 800 °C to 1200 °C, and in some other work it was 1300 °C⁸.

Disadvantage of this method is that Barium titanate powders prepared by a solid-state reaction are highly agglomerated, with a large particle size (2-5 μm) and high impurity contents due to their inherent problems such as high reaction temperature, heterogeneous solid phase reaction, which result in poor electrical properties of the sintered ceramics. To eliminate these problems, many wet chemical synthesis routes are developed to generate high purity, homogeneous, reactive ultrafine barium titanate powders at low temperatures².

➤ Hydrothermal synthesis

The hydrothermal method is attractive for synthesizing BaTiO₃ powder, because the combined effects of solvent, temperature and pressure on the ionic reaction equilibrium can stabilize desirable products while inhibiting formation of undesirable compounds. Hydrothermal synthesis also makes it possible to prepare BaTiO₃ powder in a single processing step and does not require elaborate apparatus or expensive reagents.

Ciftci et al synthesized BaTiO₃ powder by the hydrothermal method at temperatures between ~100-200⁰C by reacting fine TiO₂ particles with a strongly alkaline solution (pH>12) of Ba(OH)₂. TiCl₄, titanium alkoxide and TiO₂ gels were used as titanium sources at reaction temperatures in the range of 100-400⁰C. Hydrothermal BaTiO₃ powders have a fine particle size in the range of 50-400 nm and narrow distribution of sizes making these powders highly sinterable as well as attractive for the production of thin dielectric layers. Boulos et al synthesized BaTiO₃ powders by the hydrothermal method using two different titanium sources TiCl₃ and TiO₂. The barium source was BaCl₂·2H₂O. Synthesis was performed at two temperatures, namely 150⁰ C and 250⁰ C. SEM micrographs of barium titanate powders show spherical highly crystallized elementary grains with sizes in the range 40-70 nm for samples prepared from TiCl₃ at 150⁰ C and 80-120 nm at 250⁰ C. The average particle size for powders obtained from TiO₂ at 150⁰ C or 250⁰ C was 40-70 nm².

➤ Co-precipitation method

The co-precipitation process is a widely studied technique. This is a simple and convenient method for achieving chemical homogeneity through mixing of constituent ions on the molecular level under controlled conditions. In the case of co-precipitation by the oxalate route, it is difficult to achieve optimal conditions where precipitation of both Ba and Ti cations occurs simultaneously. This is because titanium is precipitated as titanyl oxalate at pH ≤ 2 in the presence of alcohol, and barium precipitation as BaC₂O₄ needs pH ≥ 4. So, in the pH range 2-4 titanium forms soluble anionic species like TiO(C₂O₄)₂²⁻ affecting the stoichiometry (Ba:Ti ratio) during simultaneous precipitation. Coprecipitation of barium and titanium in the form of individual oxalates has been rarely attempted. It is reported to be an innovative way of maneuvering of the chemical conditions such as pH, reagent concentration, reaction medium, chelating properties of oxalic acid, complexation with metal ions and their stability, which make it possible to coprecipitate simultaneously and stoichiometrically Ba and Ti in the form of oxalates³.

➤ Sol-Gel method

Sol-gel is a method for preparing metal oxide glasses and ceramics by hydrolyzing a chemical precursor to form a sol and then a gel, which on drying (evaporation) and pyrolysis gives an amorphous oxide. Upon further heat treatment crystallization can be induced. There are three basic steps involved: (1) partial hydrolysis of metal alkoxide to form reactive monomers; (2) polycondensation of these monomers to form colloid-like oligomers (sol); (3) additional hydrolysis to promote polymerization and cross-linking leading to a 3-dimensional matrix (gel). As polymerization and cross-linking progress, the viscosity of the sol gradually increases until the sol-gel transition point, where viscosity abruptly increases and gelatin occurs.

In the sol-gel technique, the structural and electrical properties of the final product are strongly dependent on the nature of the precursor solution, deposition conditions and the substrate.

Wang et al used two typical wet-chemistry synthesis methods, stearic acid gel and acetic acid gel. In the first method, barium acetate, tetrabutyl titanate, isopropyl alcohol and glacial acetic acid were starting reagents. 0.1 mol of tetrabutyl titanate was dissolved into isopropyl alcohol at room temperature and then 0.3 mol of glacial acetic acid was added and stirred to form a titanyl acylate compound. Next, 0.1 mol of barium acetate dissolved in an aqueous solution of acetic acid was dropped into the above compound gradually. The pH value was between 3.0-4.0 using glacial acetic acid. After stirring the mixture for 30 min., a transparent sol was obtained. Aging at 95 °C was performed until a gel formed, followed by drying at 120 °C for 12h in an oven, and finally, the dried gel was calcined in air at different temperatures to obtain BaTiO₃ nanopowders. The average particle size of this powder was from 50-80 nm. For the second method also used by Wang et al starting reagents were barium stearate, tetrabutyl titanate and stearic acid. An appropriate amount of stearic acid was first melted in a beaker at 73 °C, and then a fixed amount of barium stearate was added to the melted stearic acid and dissolved to form a yellow transparent solution. Next, stoichiometric tetrabutyl titanate was added to the solution, stirring to form a homogeneous brown sol, naturally cooling down to room temperature, and drying for 12h to obtain a gel. The gel was calcined at different temperatures in air to obtain nano-crystallites of BaTiO₃ with the size of particles from 25-50 nm. Li et al described the oxalic acid precipitation method which is very similar to the sol-gel acetate method. But acetic acid was replaced by the oxalic acid, molar ratio between oxalic acid and tetra butyl titanate was 2.2: 1; Ti solution was prepared by dissolving the tetra butyl titanate into the solution of alcohol and oxalic acid. The particle size prepared by this method was 38.2 nm².

➤ Sol-gel assisted solid phase method

Lijie Mia , Qiankang Zhanga , Haiwang Wanga,b,, Zhengjie Wua , Yongxiang Guoa , Yuanming Lia , Xinyu Xionga , Kefan Liua , Weijie Fua , Yuan Maa , BingZhu Wanga , and XiWei Q proposed a new sol-gel-assisted solid-phase method for the preparation of nano BaTiO₃ ceramics to solves the shortcomings of too high temperature in solid-phase preparation and NO₂ pollution produced by sol-gel method. In this method 5.6mL of hydrochloric acid (mass fraction 36% to 38%) and 36mL of deionized water were added to 150mL of absolute ethanol, followed by constant temperature stirring at 30°C for 20 min. This solution was called liquid A. To 37.5mL of absolute ethanol, 13.5g of butyl titanate was added, followed by stirring at 30°C for 30min at a constant temperature, and this solution was called liquid B. 7.8273g of BaCO₃ (molar ratio: tetrabutyl titanate: barium carbonate = 1:1) was added to solution B, and stirring was continued at 30°C for 20min. After that, ultrasonic treatment was performed for 50min and the power was 360W. Thereafter, the solution A was slowly added to the solution B at a rate of 5s/drop in a constant temperature water bath at 30°C until a sol was formed, and the sol was allowed to stand for 3 hours in a dark room to obtain a gel. Then, the gel was dried by heating at 80°C for 8 hours to obtain a BaCO₃/TiO₂ xerogel. After grinding, the BaTiO₃ was prepared by sintering in air at different temperatures (500,600, 700, 800, 900, 1000 and 1100°C) for 2 hours⁹.

➤ Sonochemically activated solid-state synthesis

Seung Hyun Jin , Hae Won Lee , Na Won Kim , Byung-Woo Lee , Gil-Geun Lee , Youn-Woo Hong , Woo Hyun Nam , and Young Soo Lim reported the sonochemically activated solid-state synthesis of BaTiO₃ powders. In this method, the equimolar mixtures (total 20 g, 14.2378 g of BaCO₃, and 5.7622 g of TiO₂) of the starting materials were dispersed in ethanol (150 mL) in 250 mL beakers, and then they were sonochemically mixed using an ultrasonic homogenizer with the ultrasonic power levels of 300, 400, 600, and 900 W at 20 kHz for 5 min. The diameter of the ultrasonic probe was 16 mm, and the gap between the probe and the bottom of the beaker was maintained at 15 mm. This mixture is dried in an oven at 120⁰ C and then calcined at 900–1200⁰ C in air for 3 h with a heating rate of 3⁰ C/min. The calcined powder is mixed with 1–2 wt% polyvinyl alcohol binder (PVA, Mw 85,000–124,000), and then uniaxially pressed at 100 MPa. The binder was burned out at 500⁰ C for 60 min and subsequently sintered at 1300⁰ C in air for 4h.

The sonochemical mixing can replace the time-consuming ball-mill mixing for the solid-state synthesis of BaTiO₃ powders and can also be applied to develop a time-saving, contamination-free, and cost-effective process for various ceramic industries¹⁰.

➤ Microwave assisted radiant hybrid sintering technique

V. Raghavendra Reddya , Sanjay Kumar Upadhya , Ajay Gupta , Anand M. Awasthi , Shamima Hussain reported a microwave-assisted radiant hybrid sintering for the preparation of barium titanate. For the preparation of BaTiO₃ ceramics, equimolar amount of stoichiometric BaCO₃ (99.99%) and TiO₂ (99.99%) were mixed thoroughly using acetone as a mixing medium. The mixed powder was calcined at 900 1C for 12 h. The calcined powder was then grinded for 4 h and pre-sintering was done at 1100 1C for 12 h. The resulting powder was made in to pellets of about 10 mm diameter and a thickness of 1 mm. A suitable amount of binder is added to the samples before making pellets. For final sintering, the pellets were subjected to 1200 1C for 2 h with different percentage of microwave power (0, 15, 30, 50 and 75%). y. The samples were furnace cooled to room temperature after the heat treatment.¹¹

➤ Rapid mechanochemical synthesis

Satoshi Ohara , Akira Kondo, Hirofumi Shimoda, Kazuyoshi Sato, Hiroya Abe, and Makio Naito demonstrated a rapid mechanochemical synthesis of fine BaTiO₃ nanoparticles, starting from a mixture of BaCO₃ and TiO₂. These two powders were mixed with equimolar ratio, and the powder mixture of 60 g placed into the chamber of an attrition type apparatus. . Its main components are a fixed chamber and a rotor set with a certain clearance against the inside wall of the chamber. Both the chamber and the rotor were made from stainless steel. When the rotor rotates, the powder mixture is compressed into the clearance (1 mm in gap) and receives various kinds of mechanical forces including compression and shearing giving a desired product¹².

➤ Pechini Sol-Gel Method

Yuan Ting Wu, Xiu Feng Wang, Cheng Long Yu, and Er Yuan Le synthesized, barium titanate powders via two Pechini sol-gel processes using citric acid and polyethylene glycol-6000 as chelating agents.

Route I: $\text{Ti}(\text{OC}_4\text{H}_9)_4$ solution (A) was prepared by dissolving 0.01 mol $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and 0.023 mol citric acid in 20 ml ammonia. $\text{Ba}(\text{CH}_3\text{COO})_2$ solution (B) of 0.01 mol $\text{Ba}(\text{CH}_3\text{COO})_2$, 0.023 mol citric acid, and 20 ml ammonia was obtained by stirring at room temperature. Solution (B) was added into the solution (A) (Ba=Ti molar ratio 1:1) with stirring vigorously at 70°C to prepare solution (C). Next, 10 ml ethanol and 8 ml distilled water were added to the solution (C), and 4 g PEG-6000 was dissolved into the solution to obtain sol-1. In order to promote the esterification reaction the sol was heated up to 85°C for 6 h to form gel. Then the gel was dried at 150°C for 6 h in an oven. Finally, the dried gel-1 was calcined in air at different temperatures ranging from 400°C to 720°C at a heating rate of $5^\circ\text{C}/\text{min}$.

Route II: $\text{Ba}(\text{CH}_3\text{COO})_2$ solution (B) was prepared by dissolving 0.01 mol $\text{Ba}(\text{CH}_3\text{COO})_2$ and 0.023 mol citric acid in 20 ml NH_4OH . $\text{Ti}(\text{OC}_4\text{H}_9)_4$ solution (A) of 0.01 mol $\text{Ti}(\text{OC}_4\text{H}_9)_4$, 0.023 mol citric acid, and 10 ml ethanol was obtained by stirring at 70°C . Solution (B) was added into the solution (A) (Ba=Ti molar ratio 1:1) with stirring vigorously to prepare solution (C). Next, 8 ml distilled water and 20 ml ammonia were added to the solution (C), and 4 g PEG-6000 was dissolved into the solution to obtain sol-2. BaTiO_3 powders were prepared as the same thermal process as route I¹³.

5.2. Effect of particle size on properties of Barium titanate

The particle size of the ceramic powders plays a key factor on the performance of sintered ceramic components. The particle size depends on the method of synthesis and quality of powdered material used for synthesis. The change in properties with decreasing physical dimensions is usually referred to as size effect¹⁴. The dielectric constant value of BaTiO_3 ceramics increases with decreasing average grain size, passing through a maximum of over 5000 at 0.8–1.1 micro meter, then decreasing rapidly with further decreasing average grain size. This physical phenomenon is extremely important for BaTiO_3 as a dielectric material to fabricate dielectric devices like ceramic capacitors and multilayered ceramic capacitors.

P. Zheng, J.L. Zhang, Y.Q. Tan, C.L. Wang studied the Grain-size effects on dielectric and piezoelectric properties of poled BaTiO_3 ceramics. They prepared a series of high-quality BaTiO_3 ceramics with various average grain sizes and relatively uniform grain-size distributions, using a proper TiO_2 powder as the raw material, by the conventional solid-state reaction under different sintering conditions and investigated the grain-size effects on the dielectric and piezoelectric properties of poled BaTiO_3 ceramics. It was found that dielectric permittivity and piezoelectric constant increase significantly at room temperature with reducing average grain size and both reaches their maxima at $g = 0.94$ micro meters¹⁵.

Xiaoteng Chen , Jinxing Sun , Binbin Guo , Yue Wang , Shixiang Yu, Wei Wang , Jiaming Bai fabricated , BaTiO₃ ceramic components by adopting different suspensions filled with the submicron powder particle size of 200 nm, 500 nm and 600 nm, respectively. Subsequently, investigated the effects of particle size on the rheological properties and photopolymerization behaviors of the suspensions, as well as the density, grain size, piezoelectric and dielectric properties of the ceramic components. The result indicated that the suspensions with the coarsest powder showed the lowest viscosity and the highest cure depth; when the grain size distributed in submicron range, the piezoelectric constant and relative permittivity of sintered BaTiO₃ ceramic are direct positively correlated to the grain size. The value of dielectric permittivity and piezoelectric constant were related with domain structure affected by grain size⁷.

5.3 Effect of doping on properties of Barium titanate

Barium titanate is a very attractive perovskite given its ferroelectric, piezoelectric and dielectric properties. These properties can be improved by the introduction of a large number of different dopants that can occupy both the A and B sites of BaTiO₃ perovskites. Introducing both rare earths and/or metals in this compound enhances its optical and electrical properties, thus making it a multifunctional material suitable for many different applications. Ca²⁺ substitution for Ba²⁺ results in a shift of the dielectric constant and a reduction of the Curie point due to the sensitivity of these parameters to the grain size. Researchers also found that doping of BaTiO₃ with Sn⁴⁺ affects its dielectric properties, transition temperature and causes a phase transition. The resulting material can find applications in the development of ceramic capacitors. The doping of BaTiO₃ with several chemical elements is possible, therefore offers unique opportunities to engineer the properties of the crystal in a range of applications. BaTiO₃ upon doping may modify properties such as: Curie temperature, electric permittivity, grain size as well as the refractive index, the electrooptic response and obtain light emission properties. Both acceptor and donor-type additions in BaTiO₃ have an impact on the quality of the crystal and the related properties¹⁶.

Rached , M. A. Wederni , A. Belkahla , J. Dhahric , K. Khirounia, S. Alayaa and Raúl J. Martín-Palmaid studied Effect of doping in the physico-chemical properties of BaTiO₃ ceramics. the compound Ba_{0.91}Er_{0.1/3}Ca_{0.04}Ti_{0.92}Sn_{0.08}O₃ is prepared by solid state reaction and its structural, morphological, thermal optical and electrical properties are investigated in detail by X ray diffraction, scanning electron microscopy, differential scanning calorimetric, absorption spectroscopy and impedance spectroscopy respectively. Two-phase transitions at 448 K and 572 K are deduced from thermal and electrical measurements. The optical measurements indicate that both erbium and tin are well introduced in the structure, which is confirmed by energy dispersive spectroscopy, and affects the vibrational modes. a.c. and d.c. electrical measurements show that, depending on the measurement temperature range, conduction mechanism is either a non-overlapping small polaron tunneling or a correlated barrier hopping model. . Moreover, dielectric measurements prove a high dielectric constant and identify a phase transition from the ferroelectric phase to paraelectric one which is in agreement with

literature. Such substitution improves the compound properties and makes it suitable for different devices¹⁷.

Muhammad Rizwana , Hajraa , I. Zebab , Muhammad Shakila , S.S.A. Gillanic, Zahid Usman studied Electronic, structural and optical properties of BaTiO₃ doped with lanthanum (La). . Material under study has been doped by Lanthanum (La) at the sites of Barium (Ba). Before and after doping they calculated the different optical, structural and electronic properties. After doping, reduction of band gap is noticed and as well as nature of band gap is also changed from indirect band gap (IBG) to direct band gap (DBG). Refractive index (n) is 2.598 for pure and 2.482 for doped system. Absorption peak also effected by inclusion of La. The band gap reduction is due to La-5d states which have more contribution in conduction band. All the optical properties including DF, absorption, refractive index etc. are also changed¹.

5.4. Application of Barium titanate

❖ Multilayer ceramic capacitors (MLCs)

The largest class of ceramic capacitors produced, in numbers and in value, is the multilayer type. In its simplest form, a capacitor consists of a pair of parallel metal plates separated by free space. When a voltage is applied across the plates, a charge is developed on them that are proportional to the applied voltage. If an insulating material is placed between the plates, the charge on the plates increases by the relative dielectric constant. High values of dielectric constant make BaTiO₃ ceramic a popular choice for use in capacitors. The first multilayer capacitors made from polycrystalline BaTiO₃ ceramics were produced in the early 1950s⁴.

❖ Positive temperature coefficient (PTC) thermistors

Elements based on materials with a positive temperature coefficient of resistance (PTCR) have found wide application practically in all branches of engineering. The positive temperature coefficient of resistance (PTCR) effect was found in doped semiconducting barium titanate and it is a grain boundary controlled phenomenon. Barium titanate is normally an insulator but after doping with trivalent donors (e.g. La, Sb, Y) that substitute for Ba²⁺ or with pentavalent donors (e.g. Nb, Ta) that substitute for Ti⁴⁺, BaTiO₃ becomes semiconductive. It has been established that the PTCR effect is a grain boundary resistance effect, even at temperatures well below the Curie point.

These PTC materials prepared from doped semiconducting BaTiO₃ ceramics can be used in various kinds of electronic circuitry as a switching device or as a constant temperature heater. Other important application of a PTC thermistor is the measurement/detection/control of

temperature or parameters related to temperature. These PTC materials are known to have the highest temperature coefficient of resistance among all sensor materials available.

❖ Photocatalytic oxidation of atrazine using BaTiO₃

Tariq R. Sobahi, M.S. Amin used the BaTiO₃-MWCNT nanocomposite for a photocatalytic oxidation of atrazine which is a important part of herbicide but harmful for the environment hence its elimination is crucial. They reported that the Small quantity of the upgraded nanocomposite was able to decompose AT completely when exposed to visible light for 40 min. Furthermore, the recycled catalyst was able to carry out the same photocatalytic reaction, for many times, without pronounced reduction in the photocatalytic achievement. The prepared BaTiO₃-MWCNT photocatalysts offered great stability and durability which are the requirements of the industrial application¹⁸.

❖ Gas sensor

Due to the large presence of carbon oxide gases in both our environment and industry, there is an ongoing search for simple and efficient gas sensors. As a response to the current challenges toward lower limits of detection, Igor Lukačević , Maja Varga Pajtler, Matko Mužević studied the Sensing capabilities of ultrathin BaTiO₃ nanostructures toward carbon oxides based on optical signals from the theoretical perspective. This ultra-thin sensing model predicts that sensing could be achieved by making advantage of the visible optical signals from BaTiO₃. They are demonstrated for a number of different optical properties, including absorption, reflection and electron energy loss spectra. Critical changes in the visible spectrum. When CO₂ or CO molecule absorb on this ultra thin sensor the various spectras shows a prominent changes in spectral intensities and signals thus enabling the detection of gases¹⁹.

On similar lines R.P. Patil, Priyesh V. More, G.H. Jain, Pawan K. Khanna, V.B. Gaikwad applied BaTiO₃ nanostructures for H₂S gas sensor²⁰.

❖ Photonic Applications of Barium Titanate Nanostructure

BaTiO₃ nanoparticles have been considered as probes for imaging due to their nonlinear optical properties. Most of the energy absorbed in the two-photon absorption process is transformed in nonradiative heat because BaTiO₃ is a weakly fluorescent material. This property of BaTiO₃ nanoparticles is used to develop high resolution bioimaging techniques with no fluorescent materials. One such example based on the two-photon absorption is two-photon photothermal microscopy¹⁶.

6. CONCLUSION

- Barium titanate is a member of a large family of compounds with general formula ABO_3 called perovskite.
- The most investigated phase transition is from tetragonal ferroelectric to cubic paraelectric structure which occurs at Curie point $T_c = 120^\circ\text{C}$.
- There are many methods of preparation of barium titanate is reported in the literature but the most frequently used are solid- state reaction, mechano-chemical synthesis and wet chemical methods such as sol-gel, hydrothermal, co-precipitation, polymeric precursor method.
- Particle size plays a very important role in showing the different properties for different applications.
- It can be concluded that the synthesis method has a great effect on the desired characteristics of powders and ceramics, influencing the end application.
- Doping of barium titanate with different element enhances the properties thus giving wide range of applications.
- Barium titanate is still a little understood material that will continue to fascinate researchers from many fields for a long time to come.

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