Abstract: 
Barium titanate is the first ferroelectric ceramics and a good candidate for a variety of applications due to its excellent dielectric, ferroelectric and piezoelectric properties. Barium titanate is a member of a large family of compounds with the general formula $ABO_3$ called perovskites. Barium titanate can be prepared using different methods. The synthesis method depends on the desired characteristics for the end application. The used method has a significant influence on the structure and properties of barium titanate materials. In this review paper, Part I contains a study of the $BaTiO_3$ structure and frequently used synthesis methods.

Keywords: Barium titanate ceramics, Perovskite structure, Synthesis method, Dielectric properties, Ferroelectric properties

1. Introduction

Barium titanate ($BaTiO_3$) 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 samples [1]. Due to its high dielectric constant and low loss characteristics, barium titanate has been used in applications, such as capacitors and multilayer capacitors (MLCs). Doped barium titanate has found wide application in semiconductors, PTC thermistors and piezoelectric devices, and has become one of the most important ferroelectric ceramics. The properties of $BaTiO_3$ have been reported in a number of papers. Barium titanate is a member of a large group of compounds which is called the perovskite family. Ceramic materials with a perovskite structure are very significant electronic materials. In this review paper, a study on the barium titanate structure and the most often used preparation methods is presented.

2. Ferroelectric materials in general

The phenomenon of ferroelectricity was discovered in single-crystal materials of Rochelle salt (sodium tartarate tetrahydrate, $NaKC_4H_4O_6 \cdot 4H_2O$) in 1921. The two conditions necessary in a material to classify it as a ferroelectric are (1) the existence of spontaneous polarization and (2) a demonstrated reorienting of the polarization [2]. Spontaneously polarized regions, with a single direction of polarization, are called domains. Orientation
relationships between domains are governed by the crystal symmetry. The most outstanding feature of a ferroelectric ceramic is its hysteresis loop (i.e. a plot of polarization versus electric field, P-E). Fig. 1 illustrates a typical hysteresis loop.

![Hysteresis Loop Diagram](image)

**Fig. 1.** A typical P-E hysteresis loop in ferroelectrics[3]

When we apply an electric field, dipoles which are already oriented in the direction of the field will remain so aligned, but those which are oriented in the opposite direction will show a tendency to reverse their orientation, on the hysteresis loop that is a linear relationship between P and E and crystal behaves like a normal dielectric. When the electric field becomes sufficiently high to switch dipoles in crystallites, the polarization changes sharply and reaches saturation at higher fields. When the field is reduced to zero a net permanent polarization remains in the material known as remanent polarization, \( P_R \). Extrapolation of the linear part of the curve back of the polarization axis represents the value of the spontaneous polarization, \( P_S \). Reversing the electric field, polarization is reduced to zero and then changes sign as the field produced saturation polarization in the opposite direction, completing the cycle of the hysteresis loop. The value of the field required to reduce P to zero is called the coercive field \( E_C \) [4-5].

Ferroelectric BaTiO\(_3\) has a Curie temperature of 120 °C, possesses a high dielectric constant at room temperature \( \geq 1500 \) and low dielectric loss [6]. Because of these good characteristics barium titanate nowadays has become more and more important in ceramics materials.

### 3. Barium Titanate Structure

#### 3.1. Perovskite structure

The perovskite structure is adopted by many oxides that have the chemical formula ABO\(_3\). Barium titanate is a member of this perovskite family. This structure takes it name from the mineral perovskite, CaTiO\(_3\). The general crystal structure is a primitive cube, with 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. Geometrical packing of ions in the lattice is a very important factor determining the structure type. The perovskite structure can be considered as a three-dimensional frame work of BO\(_6\) octahedra (Fig.2a), but it can also be regarded as a cubic close packed arrangement of A and O ions, with the B ions filling the interstitial positions (Fig.2b) [1,7]. The unit cell of the cubic
perovskite type lattice is shown on Fig. 2 [8]. It can be detected that the coordination number of cation A is 12 and for cation B is 6.

![Fig. 2. Cubic perovskite-type structure ABO₃ [8]](image)

The perovskite family includes not only compounds with an ideal cubic perovskite lattice, but also all compounds with structures which can be derived from the ideal one by way of small lattice distortions or omission of some atoms. For example a large number of double fluorides, such as KMgF₃, KZnF₃ and others, also belong to the perovskite family [1].

### 3.2. Structural phase transitions in barium titanate

Barium titanate is the first discovered ferroelectric perovskite. Its ferroelectric properties are connected with a series of three structural phase transitions. 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 [9]. When the temperature is below the Curie point, crystallographic changes in BaTiO₃ 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. [1,10]. Fig. 3 illustrates crystallographic changes of BaTiO₃ [1].

![Fig. 3. Unit cells of the four phases of BaTiO₃.](image)

The dotted lines in (b), (c) and (d) delineate the original cubic cell [1].
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, as shown in Fig. 4 [3].

These changes can be related to structural distorsion, lengthening of the bonds or their shortening, so crystallographic dimensions of the barium titanate lattice change with temperature [10]. A lot of papers indicate that the mechanisms responsible for these phase transitions in BaTiO$_3$ are complex.

The temperature dependence of the lattice constants of BaTiO$_3$ in the four phases is depicted in Fig. 5 [1].

4. Barium titanate synthesis methods

BaTiO$_3$ 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 [11]. 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 [2,12]. All techniques have advantages for obtaining BaTiO$_3$ ceramics with required properties.

4.1. Conventional solid-state reaction

Traditionally, barium titanate is prepared by a solid-state reaction that involves ball milling of BaCO$_3$ or BaO and TiO$_2$. The mixture has to be calcined at high temperature. In some reports the needed calcination temperature was as high as 800 $^\circ$C to 1200 $^\circ$C [13-15], and in some other work it was 1300 $^\circ$C [16]. Barium titanate powders prepared by a solid-state reaction are highly agglomerated, with a large particle size (2-5 $\mu$m) 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 [17]. To eliminate these problems, many wet chemical synthesis routes are developed to generate high purity, homogeneous, reactive ultrafine barium titanate powders at low temperatures [14].

4.2. Chemical methods for barium titanate synthesis

Chemical synthesis has grown up through techniques such as sol – gel, coprecipitation, hydrothermal and polymeric precursor method. The advantage of chemical methods is the quasi – atomic dispersion of constituent components in a liquid precursor, which facilitates synthesis of the crystallized powder with submicron particles and high purity at low temperatures. The properties of the powder may vary as different preparation methods are used [9,18]. Li et al [19] described different synthesis routes for BaTiO$_3$ preparation.

4.2.1. 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 two 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.

Step 1 – Partial hydrolysis

M(OR)$_n$ + mH$_2$O $\rightarrow$... M(OR)($_{n-m}$)(OH)$_m$ + ROH

Step 2 – Condensation

2M(OR)$_{n-m}$(OH)$_m$ $\rightarrow$...(OR)$_{n-m}$M-O-(OR)$_{n-m}$ + HOH

or

(OR)$_{n-1}$M-(OR) + (HO)-M(OR)$_{n-1}$ $\rightarrow$...(OR)$_{n-1}$M-O-M(OR)$_{n-1}$ + ROH

Step 3

3D cross-linking between (OR)$_{n-m}$M-O-(OR)$_{n-m}$ molecules
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 [5].

Wang et al [17] 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 [17] 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 [19] 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 tetrabutyl titanate was 2.2: 1; Ti solution was prepared by dissolving the tetrabutyl titanate into the solution of alcohol and oxalic acid. The particle size prepared by this method was 38.2 nm.

Recently, a sol-precipitation process was developed, which is quite similar to the sol-gel method. The advantage of this route is that it requires no further thermal treatment of the product, such as calcination or annealing due to enhance the homogeneity of crystals and crystal growth. However, single-crystal BaTiO₃ nanoparticles can be directly obtained at the low temperature of 80 °C and a strong alkaline condition rather than amorphous gel that often formed in the standard sol-gel process. From TEM examination nanoparticles with an average diameter of about 20 nm were detected [20].

4.2.2. Hydrothermal Method

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 [17].

Ciftci et al [21] synthesized BaTiO₃ powder by the hydrothermal method at temperatures between ~100-200 °C 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 100-400 °C. 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 [13] 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 150 °C and 250 °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 150 °C and 80-120 nm at 250 °C. The average particle size for powders obtained from TiO₂ at 150 °C or 250 °C was 40-70 nm.

Recently, a microwave-hydrothermal method was developed and has shown some advantages over the conventional hydrothermal route [22]. Some of the primary reasons for the growing interest in using microwaves for ceramic material synthesis are (1) cost savings due to rapid kinetics (time and energy), (2) rapid internal heating and (3) synthesis of new materials [23].

Liu et al. [23] attempted to prepare BaTiO₃ by the microwave method and evaluate its sinterability, microstructure and dielectric properties in comparison to samples prepared by conventional hydrothermal processing. Starting reagents were Ba(NO₃)₂, TiCl₄ and KOH. All chemical reactions were conducted in a microwave digestion system. The system is controlled by pressure and the parameters which were varied include pressure (and thus, temperature) and time. Conventional hydrothermal experiments were conducted in teflon-lined par bombs. After synthesis, the solid and solution phases were separated by centrifugation and the solid phases were dried. SEM analysis of powders prepared by both hydrothermal methods yielded a particle size of about 0.2 μm. Thus cubic BaTiO₃ powders can be prepared by the microwave method for 0.25 h, but in the case of conventional hydrothermal route for 2.5 h. Guo et al. [24] also compared these two methods in their work. They detected that the microwave hydrothermal method can obtain the desired BaTiO₃ powder in a shorter time and at a lower temperature (30 min, 80 °C) than the conventional hydrothermal method (5h, 150°C).

### 4.2.3. Coprecipitation method

The coprecipitation process is a widely studied technique [14,15,25]. 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 coprecipitation 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)₂⁻ affecting the stoichiometry (Ba:Ti ratio) during simultaneous precipitation. Coprecipitation of barium and titanium in the form of individual oxalates has been rarely attempted [14]. It is reported to be an innovative way of maneuvering of the chemical conditions such as pH [25], 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 oxalates.

The effect of pH, in the range 2.0-10.0, on the formation of a stoichiometric coprecipitated precursor for BaTiO₃ from potassium titanyl oxalate and barium chloride was investigated by Prasadarao et al. [25].

### 4.2.4. Polymeric precursor method

The polymeric precursor method is an extensively used polymeric route, where a solution of ethylene glycol, citric acid and metal-ions is polymerized to form a polyester-type resin. The metal ions can be immobilized in a rigid polyester network, and no segregation of cations was observed during thermal decomposition of the organic material [18]. Fig. 6 shows the procedure of BaTiO₃ synthesis based on the Pechini method [26].

The Pechini process for obtaining barium titanate (BaTiO₃) powder is described below. A titanium citrate solution was prepared by dissolving titanium tetra isopropoxide
(Ti[OCH(CH₃)]₃)₄ in a solution of ethylene glycol (HOCH₂CH₂OH). This solution was heated at T>60°C with constant stirring for 10 min. Afterwards, the solution of citric acid (HOOCC₆H₄(OH)(COOH)CH₂COOH) was added. The solution of titanium citrate was mixed and heated at 90°C. Simultaneously, a barium citrate solution was prepared by dissolving barium acetate in a citric acid solution. This solution was heated at 90°C and when it becomes transparent ethylene glycol was added. The molar ratio of citric acid to ethylene glycol was 1:4, for both citrate solutions. The temperature was raised up to 120 - 140°C, when the solution becomes solidified into a dark – brown glassy resin. Decomposition of most of the organic part was performed in an oven. The temperature regime was 200°C for 1 h and then at 300°C for 4 h, with constant stirring. When the resin incinerated, and became a black solid mass, then the material was pulverized. Calcinations were performed at 500°C for 4 h, 700°C for 3 h and 750°C for 2 h. The heating rate was 2°C/min. The agglomerates were smashed by milling. After drying at room temperature and querying cubic barium titanate powder was obtained. The flow chart for the Pechini process of BaTiO₃ is shown in Fig. 7 [26].

Fig. 6 Polymeric precursor method-Pechini process [26]
Cho et al. [18] prepared barium titanate by heat-treating polymeric precursors containing barium and titanium in air at 600 °C for 8h. The experimental procedure used is very similar to the one described above. They obtained cubic barium titanate powder with particles of about 20 nm. An increase in the heat-treatment temperature to 900 °C generates grain growth, resulting in BaTiO₃ particles several hundreds of nanometers in size. Vinothini et al. [12] also prepared barium titanate by the Pechini type reaction route and they obtained very similar results.

![Flow chart for the Pechini process of BaTiO₃](image)

**Fig. 7** The flow chart for the Pechini process of BaTiO₃ [26]

When coprecipitation and hydrothermal methods were used, stoichiometric deviations and formation of biphasic solid solution were reported. Also the sol-gel method and metallo-organic decomposition require a high temperature for achieving a complete solid solution. The advantage of the polymeric precursor method is based on the fact of its simplicity for obtaining powders of high purity and possibility to hold the initial stoichiometry. This method is not the best choice for industry due to long duration of the preparation process and high amounts of organic materials.

### 4.3. Mechanochemical synthesis

Mechanical activation is a very effective method for obtaining a highly dispersed system as due to mechanical action stress fields form in solids during the milling procedure [27]. During milling, heat is released, new surfaces and different crystal lattice defects are formed and a solid-state reaction is initiated. The accumulated deformation energy is the key of understanding the route of irreversible changes of the crystal structure and consequently microstructure, causing changes of material properties [27-29].

Mechanochemical synthesis of barium titanate has been the subject of research of many authors. Stojanovic et al [29] prepared BaTiO₃ starting from barium oxide (BaO)
obtained from thermally treated BaCO$_3$, according to the following reaction BaCO$_3$ $\rightarrow$ BaO + CO$_2$ in air at 900 °C/4h, and titanium oxide (TiO$_2$) in a rutile crystal form. Mechanochemical activation, i.e. mechanochemical synthesis was performed in a planetary ball mill in an air atmosphere for up to 4h, using a zirconium oxide vial and zirconium oxide balls as the milling medium. They identified strong agglomeration of powders after milling for 4h. BaTiO$_3$ powder consisted of particle agglomerates of varying size and morphology, with grains of a mostly rounded shape in the range of 20-50 nm.

Mechanical treatment of ceramic powders can reduce particle size and make it possible to obtain nano-structured powders, which are very important for preparing nanosized oxides and compounds, superconductors, ferroelectric powders etc. [5]. This method can be very useful for industrial application.

5. Summary

Barium titanate is a member of a large family of compounds with general formula ABO$_3$ called perovskite. The general crystal structure is a primitive cube, with the Ba-larger cation in the corner, the Ti-smaller cation in the middle of the cube and oxygen, in the centre of the faces edges. Barium titanate is the first discovered ferroelectric perovskite. Its ferroelectric properties are connected with a series of three structural phase transitions. The most investigated phase transition is from tetragonal ferroelectric to cubic paraelectric structure which occurs at Curie point $T_c=120$ °C.

The most frequently used synthesis methods for BaTiO$_3$ powder preparation are solid-state reaction, mechanochemical synthesis and wet chemical methods such as sol-gel, hydrothermal, coprecipitation, polymeric precursor method. It can be concluded that the synthesis method has a great effect on the desired characteristics of powders and ceramics, influencing the end application.

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Садржај. Баријум титанат је први откривени фероелектрични материјал и добар кандидат за велики број апликација захваљујући његовим одличним диелектричним, фероелектричним и пиезоелектричним особинама. Баријум титанат припада перовскитној групи јединица опште формуле $ABO_3$. Баријум титанат се може синтетизовати користећи различите методе. Изабрана метода зависи од захтеваних карактеристика за крајњу апликацију. Утврђен је значајан утицај примене методе на структуру и својства баријум титанатног материјала. У првом делу овог прегледног рада дати је анализи структуре и најчешће коришћених метода синтезе.

Кључне речи: Баријум титанатна керамика, Перовскитна структура, Методе синтезе.