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History and Challenges of Barium Titanate: Part II

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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 which is called perovskite. Barium titanate can be prepared using different methods. The synthesis method depends on the desired characteristics for the end application and the method used has a significant influence on the structure and properties of barium titanate materials. In this review paper, in Part II the properties of obtained materials and their application are presented.

Keywords: *Barium Titanate Ceramics, Perovskite structure, Synthesis method, Dielectric properties, Ferroelectric properties*

1. Introduction

Barium titanate ($BaTiO_3$) 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 ceramics.

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. Details about synthesis and processing of barium titanate were presented in Part I of this review paper. In this paper, the electric, dielectric and piezoelectric characteristics and applications of $BaTiO_3$ ceramics were studied.

2. Electric Properties of $BaTiO_3$

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.

The ferroelectricity is fundamentally associated with the domain structure and domain motion. The domain structure is formed during the cubic (paraelectric phase) to tetragonal

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phase (ferroelectric phase) transformation at Curie temperature. The configuration and type of domains depend on the presence of additives and on the microstructure obtained during the sintering process. The homogeneous and small grained microstructure with a single domain structure enables the stable and uniform ferroelectric behavior of $BaTiO_3$ ceramics. In the case of a course grained microstructure apart from the single domain, the banded is the predominate structure which affects the ferroelectric properties, the permittivity becomes inhomogeneous within the crystal [1]. Besides crystallographic modification, external strain in grains also has a great influence on the domain structure, where the grain size (microstructure) is a very important parameter which has an influence on the domain width and domain energy.

In the tetragonal phase two types of domain walls are found. The first type of ferroelectric domains are polarized perpendicularly to each other and the type of domain wall that separates this type of domain is called the "90^o wall". When the polar axes are perpendicular to the plane of the plate, the domain is called a "c" domain and when it lies within the plane of the plate, the domain is called an "a" domain (with parallel extinction).

The second type of domains is polarized antiparallel to each other and such domains are called 180^o domains, and the wall separating them is called the "180^o wall". Fig. 1 shows domain arrangements in a plate of tetragonal $BaTiO_3$ [2].

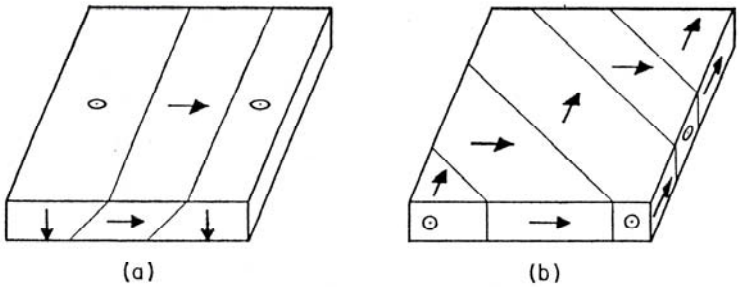

Fig. 1 Domain arrangements in an (001) plate of tetragonal $BaTiO_3$. Arrows represent the direction of the polar axis. The plate surface shows: (a) "a" domain between two "c" domains, (b) "a" domains only [2].

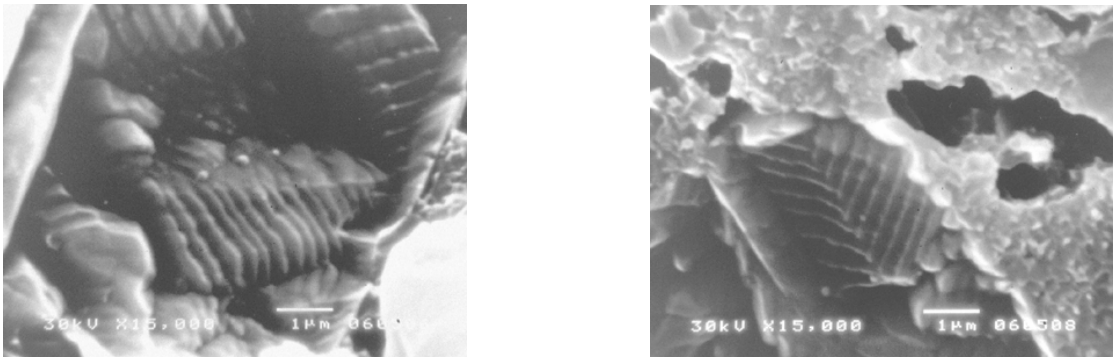

Fig. 2 SEM micrograph of domain structure in sintered samples of $BaTiO_3$ sintered at 1300^{o}C for 2h [5]

The domain structure of barium titanate has been investigated a lot [1,3,4]. In fine-grained materials showing grain size of about 1μm the domains are only visible in the SEM after chemical etching [4]. In sintered samples of $BaTiO_3$ (T_s =1300 ^{o}C for 2h), prepared by the Pechini process and chemically etched, a tetragonal phase and two types of domain

configuration were detected. The fine parallel lines were identified as 90° walls (Fig. 2.a) and the herringbone pattern (Fig. 2.b) which is described as 180° walls separating the regions with different polarization [1]. The wall thickness ranged from 0.08 μm up to 0.14 μm and from 0.14 μm up to 0.17 μm for 90° and 180° domains, respectably. The domain width was around 0.20 μm for both types of domains [5].

Therefore, it is of great interest to obtain the uniform small grained microstructure with a single domain grain structure.

2.1. Dielectric properties

$BaTiO_3$ 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 [6]. The dielectric constant is also dependent on temperature, frequency and dopants. Fig. 3 shows the temperature dependence of the dielectric constant measured with a small field along the pseudo-cubic edge [2]. In this figure, only the values of the dielectric constant in the tetragonal phase have a clear meaning, as they were measured on carefully selected single-domain crystals with the proper orientation.

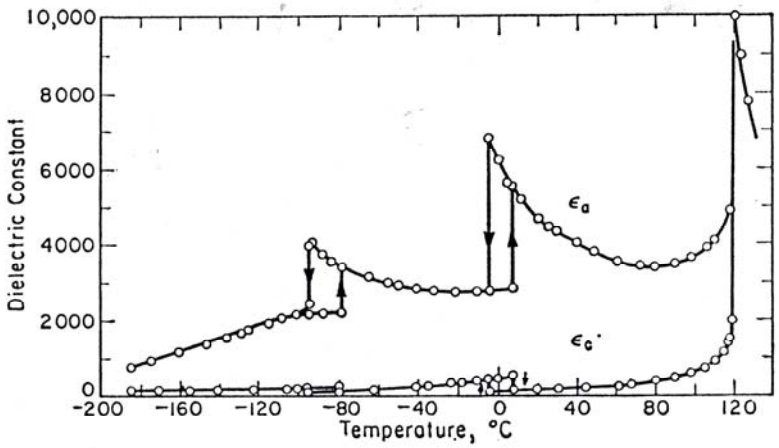

Fig. 3 Dielectric constants of $BaTiO_3$ as a function of temperature [2]

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. Values of dielectric constants of $BaTiO_3$ ceramics obtained with a different synthesis route, measured at room and Curie temperature are given in Tab. I.

Kim et al. [15] reported in their work the influence of grain size on the dielectric constant value. They prepared barium titanate powder by the Pechini process and obtained powders with various grain sizes, from 0.86 to 10 μm and measured the temperature dependence of the dielectric constant. At room temperature the dielectric constant was 4500 and 1800 and at the Curie point 6200 and 7000, for 0.86 μm and 10 μm grains, respectively. They concluded that as the grain size increased, the dielectric constant decreased at most studied temperatures, and they determined that the specimen with grain sizes of 0.86μm exhibited the highest dielectric constant for the temperature range below the Curie point. Boulos et al. [8] also investigated the influence of grain size on the dielectric constant, but in their case barium titanate ceramics was prepared by the hydrothermal method.

Tab. I Dielectric constants of $BaTiO_3$ obtained with a differenc synthesis route
*Data wasn`t published

Paper	Synthesis method	T_s (^oC)	Dielectric constant at T_{room}	Dielectric constant at T_{Curie}	frequency
Arya et al. [7]	sol-gel	1200/1300 20 min.	500-650/ 700-900	*	1MHz
Boulos et al. [8]	hydrothermal	1250/2h	2000	7000	1kHz
Xu et al. [9]	hydrothermal	900/2h	6900	11000	*
Vinothini et al. [10]	Pechini	1300/3h	1700	2840	1kHz
Duran et al. [11]	Pechini	1260/1-5h	≥ 5000	10000	1kHz
Stojanovic et al.[12]	mechanochemical	1330/2h	2500	7500	100kHz
Buscaglia et al. [13]	precipitation	1310/*	665	880	10kHz
Seveyrat et al. [14]	Oxalate coprecipitation	1350/4h	2200	8000	1,10,100 kHz

They concluded that the dielectric constant increases as the grain size is reduced from 10μm to 1μm, so the results are mainly related to the grain size and to the grain size distribution.

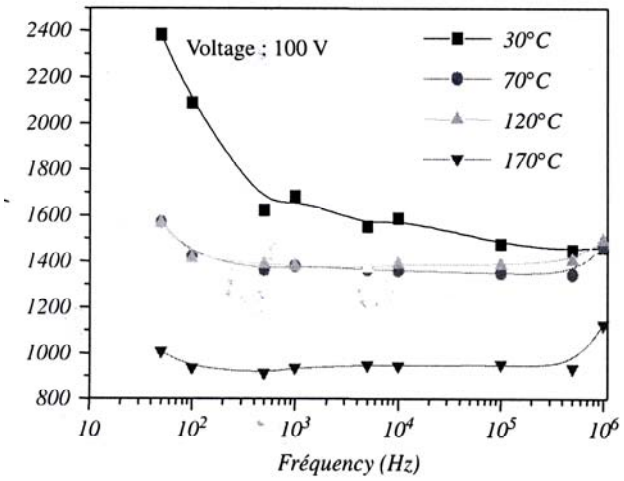

Fig. 4 Frequency dependence of relative dielectric constant in pure $BaTiO_3$ [16]

Benlahrache et al. [16] show results obtained by measuring the frequency dependence of the dielectric constant (Fig. 4) in pure $BaTiO_3$ prepared by the conventional procedure of milling and calcination. Measurements were performed of samples sintered at 1500 ^oC for 2h with the applied bias of 100 V. At the room temperature the dielectric constant decrease for frequencies below 1kHz, but for higher frequencies the dielectric constant changes slightly and tends towards a constant value. At higher temperatures, the dielectric constant decreases.

The temperature dependence of the dielectric constant and also other properties can be modified by forming a solid solution over a wide range of compositions. The perovskite structure, has the capability to host ions of different size, so a large number of different dopants can be accommodated in the $BaTiO_3$ lattice. For many years, A- and B-site dopants have been used to modify the electrical properties of $BaTiO_3$ [17]. Acceptor dopants are usually monovalent, divalent and trivalent ions which substitute Ba^{2+} and barium titanate becomes a p-type semiconductor but substitution of Ti^{4+} ions with donor dopants, trivalent, tetravalent and pentavalent ions barium titanate becomes a n-type semiconductor. Addition of donor dopants at a relatively low concentration leads to room-temperature semiconducting ceramics whereas higher dopant contents lead to insulating materials. For example substitution of Pb^{2+}, Sr^{2+}, Ca^{2+} and Cd^{2+} can be made for part of the Ba^{2+} ions, maintaing the ferroelectric characteristics. Similarly, the Ti^{4+} ion can be partially replaced with Sn^{4+}, Hf^{4+}, Zr^{4+}, Ce^{4+} and Th^{4+} [18].

2.2. Piezoelectric properties

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. The direct effect (designed as a generator) is identified with the phenomenon whereby electrical charge (polarization) is generated from a mechanical stress, whereas the converse effect (designated as a motor) is associated with the mechanical movement generated by the application of an electric field. The piezoelectric properties of ferroelectric ceramics are characterised by k_P, k_{33}, d_{33}, d_{31} and g_{33}. The piezoelectric efficiency is measured in terms of a *coupling coefficients* (k_P, k_{33}), indicating the friction of applied mechanical force converted into an electric voltage.

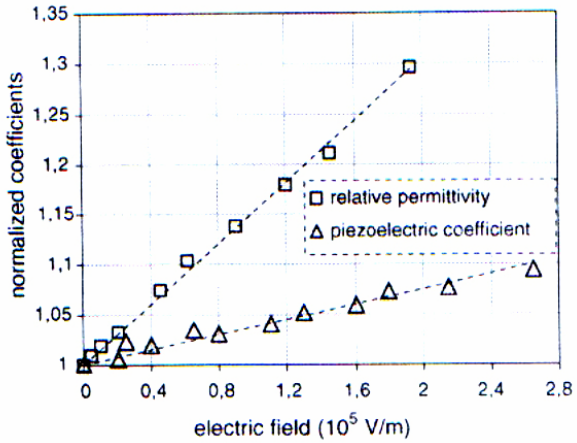

Fig. 5 Electric field dependence of both ε_r and d_{33} for $BaTiO_3$ obtained by oxalate co precipitation route and measured at 1kHz [14]

Barium titanate prepolarized ceramics have the advantage of a high coupling coefficient and at the same time are mechanically and thermally stable. The k is always less than unity and higher k values are most desirable and constantly sought after in new materials. The d coefficients are usually expressed as $\times 10^{-12}$ C/N for the direct effect and $\times 10^{-12}$ m/V for the converse effect. Higher d coefficients are desirable for those materials that are utilized in motional or vibration devices, such as sonar and sounders. g coefficients are also used to

evaluate piezoelectric ceramics for their ability to generate large amounts of voltage per unit of input stress (V· (m/N)). Higher-*g*-constant ceramics are usually ferroelectrically hard materials that do not switch their polarization readily and possess lower relative dielectric constant values. They are used in devices such as portable gas ignitors and patio lighters. Some typical values of k_P, k_{33}, d_{33}, d_{31} and g_{33} for $BaTiO_3$ are 0.36, 0.5, 190, -78 and 11.4, respectively [2,19,20,21]. Barium titanate can be manufactured in a variety of shapes and subsequently polarized in order to obtain optimum efficiency as piezoelectric elements. Since the Curie temperature of barium titanate is relatively high, piezoelectric properties are maintained, and barium titanate can be used for these purposes, at temperature as high as 70 °C. Seveyrat at al. prepared $BaTiO_3$ by conventional solid state reaction and oxalate co precipitation route and they measured electric field dependence of relative permittivity and piezoelectric coefficient d_{33}. Their results are presented on Fig. 5 [14]. They concluded that powder from a chemical process is made of finer grains and leads to ceramics with very good properties. The piezoelectric d_{33} constant is more than 260 pC/N at around 25 °C. This value is higher than the usually published values for barium titanate ceramics: classically room temperature ε_r (1kHz) and d_{33} values are respectively around 1700 and 190 pC/N [14].

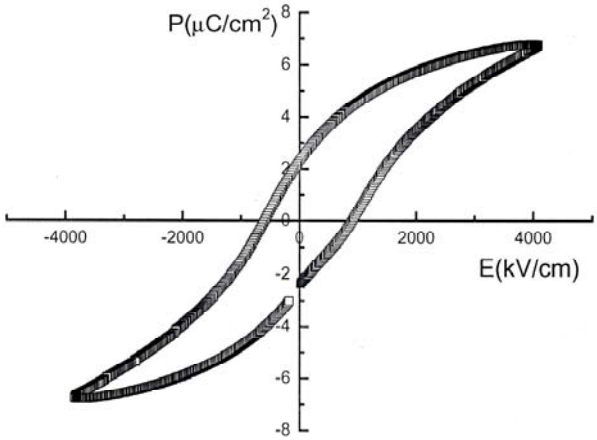

Fig. 6 The hysteresis loop of samples $BaTiO_3$ at room temperature [12]

Stojanovic et al. [12] obtained a very well performed loop with regular shape typical for ferroelectric materials. They prepared barium titanate by mechanochemical synthesis. The remanent polarization was 2.0 μC/cm^2 and coercitive field was 1060 kV/cm. The hysteresis loop is presented in Fig. 6.

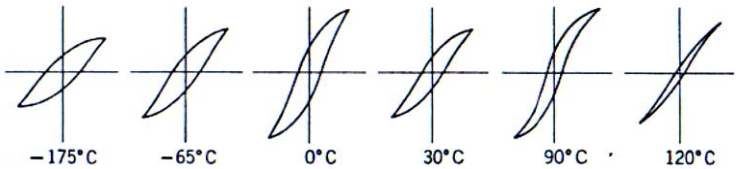

Fig. 7 The change in barium titanate ferroelectric hysteresis loop shape with temperature [18]

At low temperatures the hysteresis loops becomes fatter, and the coercitive field becomes greater, corresponding to a larger energy required to reorient the domain walls; that is, the domain configuration is frozen in. At higher temperatures the coercive force decreases until at the Curie temperature no hysteresis remains, and there is only a single value for the dielectric constant. Hysteresis loops for barium titanate, are illustrated in Fig. 7 [18].

3. Application

During the years, barium titanate based ceramics found wide application in all the areas of engineering. The most interesting applications are represented as follows.

3.1. 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 $BaTiO_3$ ceramic a popular choice for use in capacitors. The first multilayer capacitors made from polycrystalline $BaTiO_3$ ceramics were produced in the early 1950s. A multilayer ceramic capacitor is depicted on Fig. 8 [22].

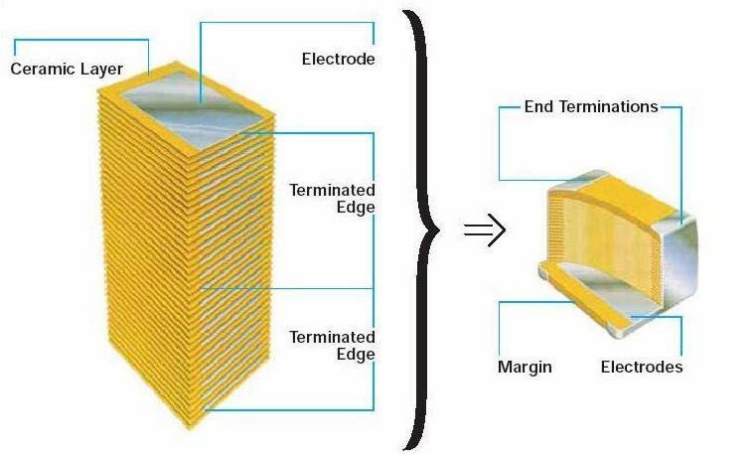

Fig. 8 Multilayer ceramic capacitor [22]

Due to growing requirements for miniaturization, the multilayer capacitor structure enables the maximum capacitance available from a thin dielectric to be packed into the minimum space in a mechanically robust form [23]. Multilayer ceramic capacitors possessing high capacitance of 1-100 μF can be engineered into passive components in circuits for LSI, replacing the widely used tantalum capacitors and aluminum electrolytic capacitors. Recently, nickel (Ni) and copper (Cu) internal electrodes have been increasingly produced to replace the expensive Ag-Pd electrodes, due to demand of cost reduction. The so-called base metal-electrode process requires a nonreducible $BaTiO_3$ dielectric that can be fired in a reducing atmosphere to prevent the electrodes from oxidation. In recent years, MLCs with Ni internal electrodes, which are composed of 500 or more laminated thin dielectric layers of ~2 μm, have been produced [24].

3.2. 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 [25]. 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 Ba^{2+} or with pentavalent donors (e.g. Nb, Ta) that substitute for Ti^{4+}, $BaTiO_3$ becomes semiconductive [23]. It has been established that the PTCR effect is a grain boundary resistance effect, even at temperatures well below the Curie point. The grain-boundary model given by Heywang treats the grain boundary as a n-type Shottky barrier with deep acceptor states at grain boundaries. The resistance anomaly behavior of doped $BaTiO_3$ is shown in Fig. 9 [26].

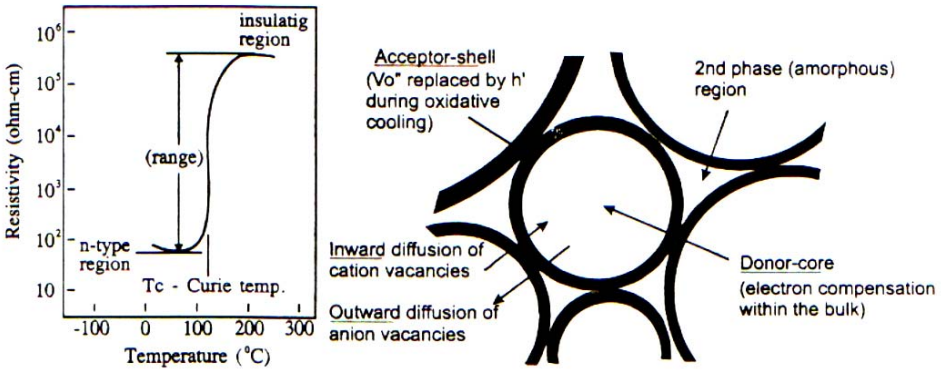

Fig. 9 Electrical resistivity for typical PTCR device and schematic presentation of defect chemistry responsible for PTCR effect [26]

These PTC materials prepared from doped semiconducting $BaTiO_3$ 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 [27].

4. Summary

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 ^oC. The ferroelectricity is fundamentally associated with domain structure and domain motion. The domain structure is formed during the cubic (paraelectric phase) to tetragonal phase (ferroelectric phase) transformation at the Curie temperature. The values of the dielectric constant depend on the synthesis route, temperature, frequency and dopants. The synthesis method depends on the desired characteristics for the end application.

Due to its high dielectric constant and low dielectric loss characteristics, barium titanate can be used as capacitors, multilayer capacitors (MLCs) and energy storage devices. Doped barium titanate has found wide application in semiconductors, PTC thermistors and piezoelectric devices.

Acknowledgements

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Абстракт: *Баријум титанат је први откривени фероелектрични материјал и добар кандидат за велики број апликација захваљујући његовим одличним диелектричним, фероелктричним и пиезоелектричним особинама. Баријум титанат припада перовскитној групи једињења 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 примењене методе*

на структуру и својства баријум титанатног материјала. У другом делу овог прегледног рада приказана су својства баријум титаната и његова најчешћа примена.
Кључне речи: *Баријум титанатна керамика, диелектричне особине, фероелектричне особине.*