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Barium titanate as a ferroelectric and piezoelectric ceramics

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Abstract: Barium titanate is a member of a large family of compounds with the general formula ABO_3 called perovskites, as the crystal size of barium titanate increases and at critical crystalline size crystal structure of barium titanate transformed from cubic to tetragonal. Transformation of crystal structure is also take place at Curi temperature. Cubic structure show paramagenatic behavior while tetragonal is ferroelectric. Differant methods of synthesis result in to the different crystalline size of barium titanate crystal structure. In ferroelectric phase barium titanate provide its great importance in the field of technology and have an amount of application due to its excellent dielectric, ferroelectric and piezoelectric properties. In this review paper, a study on variation of critical crystalline size of barium titanate and its ferroelectric and piezoelectric behavior is presented.

Key words: Barium titanate ceramics; ferroelectricity; piezoelectricity; structure and phase transitions; synthesis.

1. Introduction

Ferroelectric materials have broad applications in transducers, actuators, capacitors, and memories. Particularly well studied is $BaTiO_3$, which has rhombohedral (R), orthorhombic (O), tetragonal (T), and cubic (C) phases. The cubic structures are paraelectric while the tetragonal, orthorhombic and the rhombohedra forms are ferroelectric in nature. At the Curie temperature (around 120 ºC) paraelectric cubic $BaTiO_3$ transforms into the ferroelectric tetragonal structure, which is important parameter relating to its dielectric application. The dielectric and ferroelectric properties of $BaTiO_3$ are known to correlate with size, and the technological trend toward decreasing dimensions makes it of interest to examine this correlation when sizes are at the nanoscale[1–3]. 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. In this review paper, a study on variation of critical crystalline size of barium titanate and its ferroelectric and piezoelectric behavior is presented.

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Ferroelectric ceramics were born in the early 1940s with the discovery of the phenomenon of ferroelectricity as the source of the unusually high dielectric constant in ceramic barium titanate capacitor. Ferroelectrics are materials which show electric polarization in the absence of an external applied electric field and direction of the polarization may be reversed by an electric field. If the "centers of gravity" of the positive and negative charge distributions within a volume of material do not coincide, the material is said to have an electric dipole moment. The net dipole moment per unit volume is defined as the spontaneous polarization which is magnitude of polarization within a single ferroelectric domain in the absence of an external electric field. Spontaneous polarization is a fundamental property of all pyroelectric crystals, but it is reversible and reorientationable in ferroelectrics only. Most ferroelectric phase originates from a non-polar prototypic phase and all of the polarization is reorientationable. Its magnitude in a single crystal is directly related to the atomic displacements that occur in ferroelectric reversal and may be calculated from the atomic positions within the unit cell if know. The ferroelectricity disappears above a critical temperature Tc, called as Curie temperature, above which it behave paraelectric. Spontaneous polarization in ferroelectric state is associated with Spontaneous electrostrictive strain in the crystal. Ferroelectric state show lower symmetry then paraelectric state. At the transition temperature crystal structure is changed[4]. Ferroelectric material with high dielectric constant show high volumetric efficiency (capacitance per unit volume). $BaTiO_3$, based ceramics having a perovskite type structure show dielectric constant values as high as 15,000 as compared to 5 or 10 for common ceramic and polymer materials. The high dielectric constant $BaTiO_3$ ceramic based disk capacitors are simple to make and have captured more than 50% of the ceramic capacitor market. The volumetric efficiency can be further enhanced by using multilayer ceramic

(MLC) capacitors. Ferroelectric thin films have attracted attention for applications in many electronic and electro - optic devices. Some of the important ferroelectric materials being used for making thin films include the perovskite type materials such as $BaTiO_3$, $PbTiO_3$ etc. Applications of ferroelectric thin films utilize the unique dielectric, piezoelectric, pyroelectric sand electro- optic properties of ferroelectric materials.

Piezoelectricity refers to the generation of electricity or of electric polarity in dielectric crystals when subjected to mechanical stress and conversely, the generation of stress in such crystals in response to an applied voltage. Cady[5] defines piezoelectricity as "electric polarization produced by mechanical strain in crystals belonging to certain classes, the polarization being proportional to the strain and changing sign with it." In 1880, the Curie brothers found that quartz changed its dimensions when subjected to an electrical field and generated electrical charge when pressure was applied. Since that time, researchers have found piezoelectric properties in hundreds of ceramic and plastic materials. Many piezoelectric materials also show electrical effects due to temperature changes and applied, symmetry of crystal lost, and a net dipole moment is created. This dipole moment forms an electric field across the crystal. The materials generate an electrical charge that is proportional to the pressure applied. They are used widely in sensors and actuators, such as microphones, acoustic emitters, ultrasonic sensors and emitters, and actuators. Barium titanate ($BaTiO_3$) show its application in capacitors and piezoelectric transducers. Barium titanate ceramic is important for ultrasonic transducer, mostly for fish finders. It undergoes, in cooling, cubic-to-tetragonal, tetragonal-to-orthorhombic, and orthorhombic-to-rhombohedral transformations and above the Curie point, the crystal symmetry becomes insufficient for piezoelectricity.

2. Synthesis of Barium titanate

In proveskite barium titanate, size play important role for paraelectric to ferroelectric transition below a critical size. Barium titanate nanoparticles synthesized by solvothermal method in which Precursor $BaTi(OR)_6$ was prepared by mixing with Ba(OR)2 and $Ti(OR)_4$ in benzene. $BaTiO_3$ nanoparticle prepared with particle size less than 20 nm and XRD patterns show that tetragonal and cubic phases coexist in the nanoparticles. Dielectric measurements exhibit a broad band around 70 ºC due to the low-frequency dielectric dispersion[7]. $BaTiO_3$ powder synthesized by the hydrothermal method at temperatures between ~100-200 ºC by reacting fine TiO_2 particles with a strongly alkaline solution (pH>12) of $Ba(OH)_2$. $TiCl_4$, titanium alkoxide and TiO_2 gels were used as titanium sources at reaction temperatures in the range of 100-400 ºC. Hydrothermal $BaTiO_3$ 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[8]. Wang *et al.* [9] 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 ºC was performed until a gel formed, followed by drying at 120 ºC for 12h in an oven, and finally, the dried gel was calcined in air at different temperatures to obtain $BaTiO_3$ nanopowders. The average particle size of this powder was from 50-80 nm. For the second method also used by Wang *et al.* [9] starting reagents were barium stearate, tetrabutyl titanate and stearic acid. An appropriate amount of stearic acid was first melted in a beaker at 73 ºC, 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 $BaTiO_3$ with the size of particles from 25-50 nm. Wada *et al.*[10] reported preparation of BT particle with various size with a hot uniaxial pressing method and Curi point for a grain size 58 nm was found to be at room temperature. Li *et al.* synthesized $BaTiO_3$ by the oxalic acid precipitation method which is very similar to the sol-gel acetate method. Particle size prepared by this method was 38.2 nm[11]. Barium titanate nanoparticles synthesized by 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 titan ate into the solution of alcohol and oxalic acid. The particle size prepared by this method was 38.2 nm[12]. Boulos *et al.* [2005] reported average particle size for $BaTiO_3$ powders obtained from TiO_2 at 150 ºC or 250 ºC was 40-70 nm[13], Cubic barium titanate powder with particles of about 20 nm by heat-treating polymeric precursors containing barium and titanium in air at 600 ºC for 8h. An increase in the heat-treatment temperature to 900 ºC generates grain growth, resulting in $BaTiO_3$ particles several hundreds of nanometers in size[14].

3. Results and discussion

3.1 Structure and phase transitions:

$BaTiO_3$ is member of perovskite family ABO_3. Above its Curie point (approximately 130 ºC) the unit cell is cubic. Below the Curie point the structure is slightly distorted to the tetragonal form with a dipole moment along c direction. Other transformations occur at temperatures close to 0 ºC and -80 ºC: below 0 ºC the unit cell is orthorhombic with the polar axis parallel to a face diagonal and below -80 ºC it is rhombohedral with the polar axis along a body diagonal. A typical ABO_3 unit-cell structure is given in Figure 1. The $BaTiO_3$ unit cell consists of a corner-linked network of oxygen octahedra with Ti^{4+} ions occupying sites (B sites) within the octahedral cage and the Ba^{2+} ions situated in the interstices (A sites) created by the linked octrahedra. When an electric field is applied to this unit cell, the Ti^{4+} ion moves to a new position along the direction of the applied field. Because the crystallite and, hence, the unit cell is randomly oriented and the ions are constrained to move only along certain crystallographic directions of the unit cell.

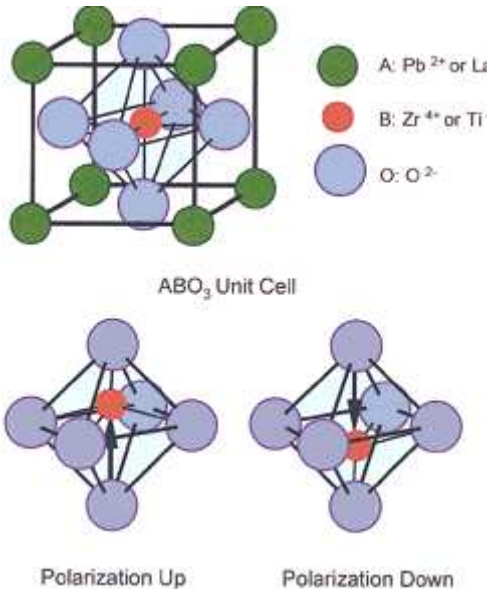

Figure 1. Perovskite ABO_3 unit cell for $BaTiO_3$ illustrating 180° polarization reversal for two of the six possible polarization states produced by displacement of the central cation in the tetragonal plane. The views of "polarization up" and "polarization down" (representing 180° polarization reversal) show two of the six possible permanent polarization positions.

$BaTiO_3$ assumes five different crystal structures namely, hexagonal, cubic, tetragonal, orthorhombic, and rhombohedral. The hexagonal and cubic structures are paraelectric while the tetragonal, orthorhombic and the rhombohedra forms are ferroelectric in nature. Figure 2 shows hexagonal $BaTiO_3$ structure is stable above 1460 ºC. Reconstructive hexagonal phase to cubic phase transformation occurs on cooling $BaTiO_3$ below 1460 ºC. Of utmost important parameter relating to its dielectric application is the ferroelectric – paraelectric transition which occurs at the Curie temperature (around 130 ºC). At this temperature, paraelectric cubic $BaTiO_3$ transforms into the ferroelectric tetragonal structure following an elongation along an edge. The tetragonal phase is stable until 0 ºC, where it transforms into the orthorhombic phase by elongation along a phase diagonal. Finally, there is a low temperature transition at – 90 ºC where the orthorhombic phase transformed to the rhombohedral phase[6].

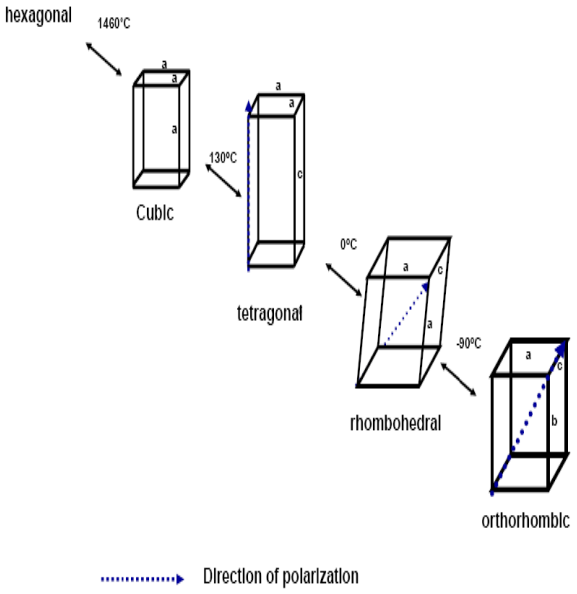

Figure 2. Phase diagram of $BaTiO_3$

3.2 Application of $BaTiO_3$ as Ferroelectric materials:

The applications for ferroelectric ceramics are covering all areas of our workplaces, homes, and automobiles. One category of applications for ferroelectric materials is that of high-dielectric-constant capacitors, particularly Multilayer capacitor (MLCs). MLCs are extremely important to our everyday lives in that they are essential to all of our currently produced electronic components, and, as such, they constitute a significant portion of the multibillion dollar electronic ceramics business as a whole. Typical applications include general-use discrete capacitors and MLCs, voltage-variable capacitors, and energy-storage capacitors[15]. Another application of ferroelectric material is $BaTiO_3$ based PTC ceramic possessing electrically conducting properties at room temperature and rather abruptly changing to a highly resistive material at some elevated temperature at Tc. Applications include switches, sensors, motor starter and controller[16]. Ferroelectric materials found applications in electrooptics and photonics due to their change in optical properties and ferroelectric polarization with

an applied electric field. By far, the largest number of applications in ferroelectric ceramics remains associated with bulk materials, but a trend toward thin and thick films for some of these applications has recently been observed and has been steadily increasing in intensity. A ferroelectric DRAM (FeDRAM) film, because of its much higher dielectric constant, occupies much less wafer area than the normal SiO_2 capacitor, thus allowing much greater capacity memories to be fabricated on a given silicon wafer[17]. Ferroelectric memories are also nonvolatile. As memories become denser in the future, the transition to ferroelectric films will become a necessity, and operating voltages for these memories will continue to decrease toward 1 V. Thin-film ferroelectrics exhibit a large decrease in dielectric constant with application of modest voltages. This suggested that they could be used as the active phase-shift elements in phased-array radar. Unfortunately, the dielectric loss tangent in these films remains too large for acceptable insertion losses in such devices.

4. Conclusions

Barium titanate is first discovered ferroelectric perovskite and a member of a large family of compounds with general formula ABO_3 . At the Curie temperature (around 120 ^{0}C) paraelectric cubic $BaTiO_3$ transforms into the ferroelectric tetragonal structure and also at critical crystalline size crystal structure of barium titanate transformed from cubic to tetragonal. Critical crystalline size of Barium titanate depends on the synthesis route, temperature and dopants etc. Differant methods of synthesis result in to different nanoscale crystalline size. In tetragonal structure it act as ferroelectric, piezoelectric and show high dielectric constant . Due to its ferroelectric properties and 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.

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