

SYNTHESIS, STRUCTURE, PROPERTIES AND APPLICATIONS OF BARIUM TITANATE NANOPARTICLES

P. Geetha¹, P. Sarita², D. Krishna Rao¹

¹Physics Department, GMR Institute of Technology, Rajam, AP, (India)

²Physics department, GIT, GITAM University, Visakhapatnam, AP, (India)

ABSTRACT

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. In this review paper, a study of the $BaTiO_3$ structure and frequently used synthesis methods. The ferroelectricity observed in barium titanate is utilized in memory applications, i.e. RAMs. The pyroelectricity and piezoelectricity are also used in the passive infrared detectors and Sonars (Sound Navigation and Ranging). In the present study, various electrical properties of barium titanate based ceramics were explained and examples of the relevant applications were given.

Keywords: Applications Of Ferroelectric Nano Particles, Barium Titanate Ceramics, Ferroelectric Properties, Perovskite Structure, Piezoelectric Properties, Synthesis Method

I. INTRODUCTION

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. $BaTiO_3$ has become one of the most important electroceramic materials among all the ferroelectric materials. $BaTiO_3$ -based ferroelectrics transform from paraelectric phase to ferroelectric phase at Curie temperature (T_c 130⁰C). The discovery of barium titanate is most significant in that it is useful from the technological point of view. Barium titanate as one of the ferroelectric materials corresponding to ferromagnetic materials is opening up new fields of technology with their very promising future. It was used at first as dielectrics, i.e. condenser materials, and has now established its indisputable position as condenser materials for high frequency circuits. Therefore, it is now beginning to be used for electro-mechanical transducers or electro-acoustic transducers and will surely gain very wide fields of application in future. This report is an outline of the characteristics and applications of barium titanate. The enormously broad range of materials exhibiting ferroelectricity and the variety of their physical properties result in numerous applications of bulk ferroelectrics.

II. BARIUM TITANATE STRUCTURE

2.1. Perovskite structure

Barium titanate is a member of this perovskite family. This structure takes its 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 unit cell of the cubic perovskite type lattice is shown on Fig.1 [1]. It can be detected that the coordination number of cation A is 12 and for cation B is 6.

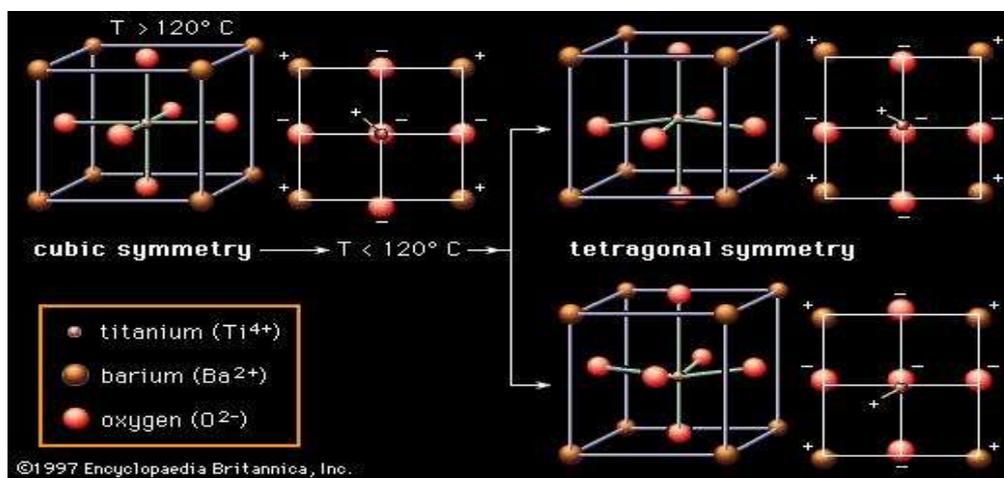


Fig.1 Cubic, tetragonal perovskite-type structure ABO₃ [1]

III. SYNTHESIS OF BARIUM TITANATE

Barium titanate nanoparticles synthesized by solvothermal method in which precursor $\text{BaTi}(\text{OR})_6$ was prepared by mixing with $\text{Ba}(\text{OR})_2$ and $\text{Ti}(\text{OR})_4$ 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. BaTiO_3 powder synthesized by the hydrothermal method at temperatures between ~ 100 - 200 °C by reacting fine TiO_2 particles with a strongly alkaline solution ($\text{pH} > 12$) of $\text{Ba}(\text{OH})_2 \cdot \text{TiCl}_4$, Hydrothermal BaTiO_3 powders have a fine particle size in the range of 50-400 nm and narrow titanium alkoxide and TiO_2 gels were used as titanium sources at reaction temperatures in the range of 100-400 °C distribution of sizes making these powders highly sinterable as well as attractive for the production of thin dielectric layers [2]. Wang et al. [3] 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. [3] 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 12 h 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. Wada et al. [4] 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 BaTiO₃ 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. 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 titanate into the solution of alcohol and oxalic acid. The particle size prepared by this method was 38.2 nm [5]. Boulos et al. [2005] reported average particle size for BaTiO₃ powders obtained from TiO₂ at 150°C or 250 °C was 40-70 nm [6] , Cubic barium titanate powder with particles of about 20 nm by heat-treating polymeric precursors containing barium and titanium in air at 600°C for 8 h. An increase in the heat-treatment temperature to 900 °C generates grain growth, resulting in BaTiO₃ particles several hundreds of nanometers in size [7].

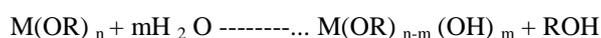
3.1. Chemical methods for barium titanate synthesis

Chemical synthesis has grown up through techniques such as sol – gel, co-precipitation, method. The properties of the powder may vary as different preparation methods are used [8]. Li et al [9] described different synthesis routes.

3.1.1. Sol-Gel method of BaTiO₃ preparation

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



Step 2 – Condensation



or



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. Wang et al [10] 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 [10] 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 [9] 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 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 [11].

3.1.2. Co-precipitation method

The co-precipitation process is a widely studied technique [12, 13, 14]. 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 $pH \leq 2$ in the presence of alcohol, and barium precipitation as BaC₂O₄ needs $pH \geq 4$. 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. Co-precipitation 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 [14], reagent concentration, reaction medium, chelating properties of oxalic acid, complexation with metal ions and their stability, which make it possible to co precipitate 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 Prasada rao et al. [14].

IV. FERROELECTRIC PROPERTIES OF BARIUM TITANATE

Amongst other ferroelectric materials, barium titanate (BaTiO₃) is a useful and technologically important material owing to its ferroelectric behavior at and above room temperature (T_c , 393⁰K), and having polarization (P_s) values several orders higher than the potassium dihydrogen phosphate-type ferroelectrics[15]. In order to improve the electrical reliability of barium titanate, nano-sized second phases were incorporated into matrix. Dielectric constant, ϵ_r was 3279, which increased with additive and dielectric loss, $\tan \delta$ remained constant. BaTiO₃ ceramic showed a slim ferroelectric loop with 4.55 kV/cm of E_c , 3.72 μ C/cm² of P_r and 0.59 of loop squareness (R_{sq}). In an attempt to improve the dielectric properties, microwave sintering was used. As a result, ϵ_r and $\tan \delta$ were measured as 2500 and 0.03, respectively. The sharpness of the P–E hysteresis loop indicates the better homogeneity and crystallinity of the prepared system. P_r and E_c are 6 μ C/cm² and 1.45 kV/cm, respectively. Al doped and undoped barium titanate indicated P_r of 11.4 and 5 μ C/cm² and E_c of 4 and 3.1 kV/cm. The dielectric constant increased and dielectric loss factor decreased by doping. However, Curie transition shifted to lower temperature (from 121 to 113⁰C).

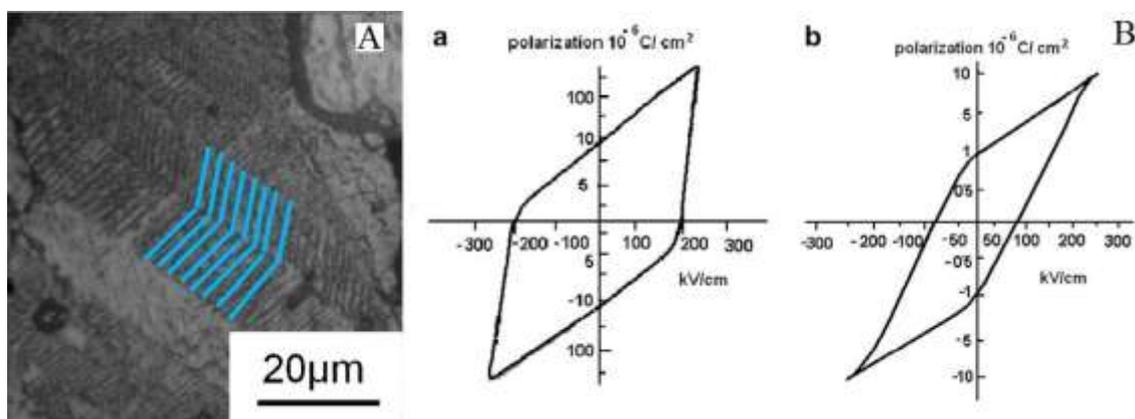


Figure 3 A. Ferroelectric domain pattern of BaTiO₃ [20] and B. Hysteresis loop of a. pellet form and Dispersed[15].

The effect of sintering temperature on the ferroelectric properties was also investigated. When the sintering temperature was raised, Curie transition shifted to higher temperature (125⁰C). The improved densification resulted in the reduction of cavities, thereby the dielectric constant increased. E_c and E_c are 10.2 μ C/cm² and 6.4 kV/cm, respectively. The remanent polarization, P_r first increased and then decreased with sintering temperature while coercive field, E_c increased continuously. However, oxygen vacancies were easier created at high sintering temperature, which strengthen the pinning effect to the ferroelectric domain as in Fig.4.A under an electric field, thereby inducing a continuous increase of the E_c and a decline of the P_r [17].

Nano-sized barium titanate was synthesized by solid state reaction. A 100% c-oriented system gives a square loop, whereas the loop for randomly oriented grains is likely to be tilted. The hysteresis loops obtained for this study is shown in Fig.4.B. The hysteresis loop is found to be wide and stretched in the case of barium titanate nanopowders used in the form of a pellet. In contrast, the polymer-dispersed BaTiO₃ nanoparticle system showed a relatively narrow loop, with long tails at the ends. The remnant polarization (P_r) was found to be 10 times larger in the case of a compact nanoparticle system ($10 \mu\text{C}/\text{cm}^2$) compared to the dispersed nanoparticles ($1 \mu\text{C}/\text{cm}^2$). It is already known that a single-crystal BaTiO₃ system could show a P_r as large as $26 \mu\text{C}/\text{cm}^2$. The coercive fields were found to be 200 and 70 kV/cm, respectively [18].

V. PIEZOELECTRIC PROPERTIES OF BARIUM TITANATE

The BaTiO₃ based normal ferroelectrics are strong candidates for field induced piezoelectric transducers due to their large polarizations, large permittivity and the large induced strains achievable in these materials. The synthesis of BaTiO₃ by conventional solid-state reaction and oxalate co-precipitation route was carried out. The properties of the ceramics from the co-precipitation process are very good and superior to those usually published especially for the d_{33} piezoelectric coefficient. The quasi-linear relation found between d_{33} and ϵ_r corresponds to a g_{33} value of $14 \times 10^{-3} \text{Vm}/\text{N}$. In the relationship, $g_{33} = d_{33} / \epsilon_{r33}$; g_{33} is the piezoelectric voltage constant (Vm / N) is the induced electric field in direction 3 (parallel to direction in which ceramic element is polarized) per unit stress applied in direction 3, d_{33} is the piezoelectric coefficient and ϵ_{r33} is the relative permittivity of ceramic material. This is the permittivity for dielectric displacement and electric field in direction 3 (parallel to direction in which ceramic element is polarized). BaTiO₃ ceramics prepared from chemical process shows dielectric and piezoelectric coefficients superior to those of other lead free materials. The piezoelectric d_{33} coefficient shows a very good stability up to $3 \times 10^5 \text{V}/\text{m}$. The piezoelectric d_{33} constant is more than 260 pC/N at around 25°C. This value is largely higher than usually published ones for barium titanate ceramics: classically room temperature ϵ_r (1kHz) and d_{33} values are respectively around 1700 and 190 pC/N [6]. Fig.5 shows the development of strain vs. electric field (S–E) butterfly loop with a max. strain 0.13% at 25 kV/cm electric field, which confirms the piezoelectric nature of the microwave sintered BaTiO₃ samples. Piezoelectric coefficient, d_{33} , has also been calculated from converse piezoelectric effect, i.e. by using the slope of the S–E plot in the higher field region, using the relation $d_{33} = \Delta \text{Strain} \% / \Delta \text{electric field}$ at higher side. The d_{33} piezoelectric coefficient calculated from the slope of S–E plot is found to be 335 pm/V. The very high value of d_{33} piezoelectric coefficient in microwave sintered BaTiO₃ samples suggests the importance of this system for piezoelectric applications. From P–E hysteresis loop of microwave sintered BaTiO₃ samples, the coercive field (E_c) of microwave sintered BaTiO₃ samples is 1.45 kV/cm. The decrease of E_c in BaTiO₃ ceramics hints towards the easy poling process and improvement in the piezoelectric properties [8].

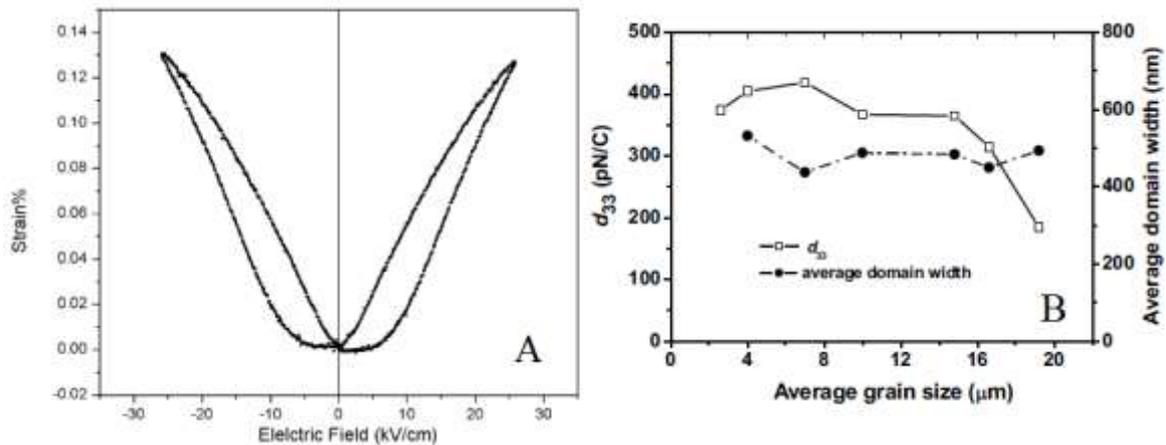


Figure 5 (A) Strain vs. bipolar electric field loop of BaTiO₃ samples [8] and (B) Changes in d_{33} and the domain width with the grain size[16]

After Al doping, d_{33} piezoelectric coefficient increased from 75 to 135 pC/N. The planar electromechanical coupling factor (k_p) also increased by Al doping. Since d_{33} and k_p are proportional to P_r , large remnant polarization resulted in high piezoelectric properties. Strains of 0.085 and 0.042% were obtained for Al doped and pure samples. The planar electromechanical coupling factor (k_p) was 1.86 and 1.53 for pure and Al doped samples [19]. The effect of sintering temperature on the piezoelectric properties was also examined. Besides the high relative density and moderate grain size, the sample sintered at 1190°C is closer to the phase transition between tetragonal symmetry and orthorhombic one, which provides a favorable condition for easier motion of domain and thus gives rise to high piezoelectric properties. This may be the main reason for the excellent piezoelectric properties of the sample sintered at 1190°C[17]. The piezoelectric constant d_{33} increased significantly at room temperature with the reduction of the average grain size and reached the maxima (338 pC/N) at 0.94 μm. The average 90 domain width decreases monotonically with grain size. Both the 90 domain wall density and the area dimension of domain wall are considered as important factors that greatly influence the d_{33} value. The piezoelectric effect in perovskite-type ferroelectric ceramics is known to be greatly influenced by the movement of the 90 domain walls. The domain walls of small area dimension will respond more actively to the external electrical or stress signal. Consequently, those BaTiO₃ ceramics with smaller grain size showed higher d_{33} values. BaTiO₃ ceramics with excellent piezoelectric properties of d_{33} 419 pC/N and k_p 0.453 have been successfully obtained using ordinary BaCO₃ and TiO₂ powders. d_{33} increases with the decrease in grain size and the domain width in the poled BaTiO₃ ceramics is nearly independent of grain size. The d_{33} change with grain size has been explained by the area change in the domain walls.

VI. APPLICATIONS OF FERROELECTRIC NANOPARTICLES IN MATERIALS TECHNOLOGIES

6.1. Ferroelectric nanoparticles in biology

In the last decade, ferroelectric nanoparticle areas of application veered toward biology and medicine. The first challenge to address when introducing nanoparticles to biological and medical systems is how to make them

stable in media that is bio-compatible, namely in aqueous solutions. If the ferroelectric nanoparticles are not coated with a stabilizing agent, the intrinsic properties of such nanoparticles very often lead to unwanted effects such as aggregation and precipitation, as well as the leaching of some ions (leading to change in particle properties) in aqueous solutions. There has been a tremendous amount of effort in the last twenty years to create many species of ferroelectric nanoparticles with different surface coatings. For example, such stabilizing agents as polyacrylic acid, polymethacrylic acid, polyaspartic acid, (aminomethyl) phosphonic acid and poly-l-lysine were tried on barium titanate nanoparticles. A large variety of possible coatings yields different surface properties of said nanoparticles – different thickness and charge of the surface layer, different strength of stabilizing agent adhesion, different resulting particle size – all of it leading to very different interactions with biological objects such as cells and cellular components. Such water-soluble ferroelectric nanoparticles can be further functionalized with fluorescent markers or antibodies [19], and they have been recently observed within a number of mammalian cells in vitro. The majority of ferroelectric nanoparticles that have been successfully functionalized are in the middle of nano size range (~100 nm or more), and the surface functionalization very frequently adds a thick surface layer, resulting in particles that are a few hundred nanometers in size. This poses a challenge which a few researchers are attempting to overcome through bio-inspired surfactants. The surface functionalization of nanoparticles can be crucial for a desired effect in a biosystem – the response is often cell-specific, and biocompatibility has to be experimentally tested for each new combination of nanoparticle and cell [20]. For example, a recent study indicates that larger (over 200 nm) barium titanate nanoparticles have been successfully used with and without surface modification and they cause no toxic response in endothelial cell cultures.

Current efforts in this area concentrate on carrying these findings through to the systems of cells and tissue in vitro.. Such biocompatible nanoparticles can be used in a variety of ways: as imaging agents, biocompatible nanoprobess, cell proliferation agents, etc. Ferroelectric nanoparticles are currently being widely explored for applications in the area of medical imaging, e.g. for enhancing contrast in second harmonic generating methods for imaging deep tissue in vitro and in vivo for such important applications as screening for genetic diseases or cancer.

6.2. Ferroelectric nanoparticles applications in medicine and medical engineering

As mentioned above, ferroelectric nanoparticles have become widely used in material science and engineering applications, but biological and medical applications of these fascinating nanoparticles has only begun to be explored in the last decade. It has been recently discovered that they can be used for cell imaging or the detection of malignancies in lung cancer studies, or they can be functionalized to induce cell proliferation [21]. Ferroelectric materials have a non-centrosymmetric crystalline structure, and are thus capable of generating a second harmonic of light. This distinctive feature of ferroelectrics is the basis for a growing number of applications of ferroelectric nanoparticles as imaging/diagnostic agents and nanoprobess in optical imaging.

Optical imaging and detection methods are the most widespread among biological and medical communities. For example, second harmonic generation imaging has been successfully used for detection of osteogenesis imperfecta in biopsies of human skin and lung cancer . To improve contrast, many of the imaging methods rely on imaging probes, such as fluorescent markers or quantum dots. This is the case for the SHG imaging

technique: the SHG signal from biological cell components is often weak, so novel nanoprobe have been introduced to enhance contrast. SHG probes are photo-stable, and do not bleach or blink unlike conventional fluorescent probes. By definition, second harmonic generating nanoprobe (such as ferroelectric nanoparticles) are capable of converting two photons of light into one photon of half the incident wavelength. This second harmonic light can be detected using methods of nonlinear optical microscopy. Nonlinear optical properties of ferroelectric nanomaterials can be used for optical phase conjugation and nonlinear microscopy. These properties have allowed them to spread to the area of medical sensors.

This also gives the ferroelectric SHG particle an edge in cell and tissue imaging in vivo. For example, recent advances in this area include imaging a tail of a living mouse with the aid of barium titanate nanoparticles.

The intrinsic large values of the dielectric permittivities of ferroelectric nanoparticles suggest their use to enhance the dielectric contrast of materials, such as polymers and references within] and biological tissue. These unique properties of ferroelectric nanoparticles lead to their novel use as contrast-enhancing agents for microwave tomography, which is a method of non-invasive assessment and diagnostics of soft tissues (such as detecting malignancies). Recently, ferroelectric electro spun nanofibers also emerged in various biomedical areas including medical prostheses, tissue engineering, wound dressing, and drug delivery .

In conclusion, ferroelectric materials found a wide variety of biomedical applications in the last decade – and the list is constantly growing. The ferroelectric material (e.g. barium titanate) used in medical implants has been known to accelerate osteogenesis , and the same material in nanoparticle form works both as an SHG probe to detect Osteo- genesis Imperfecta and, through microwave tomography, to detect lung cancer . We expect more applications will become possible if other effects, such as piezoelectricity, ferroelectric hysteresis or stress-birefringence coupling, are exploited with biology and medicine in mind.

VII. CONCLUSIONS

Barium titanate is a member of a large family of compounds with general formula ABO_3 called perovskite. 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 $T_C = 120^\circ\text{C}$. The most frequently used synthesis methods for $BaTiO_3$ powder preparation are solid- state reaction, mechano-chemical synthesis and wet chemical methods such as sol-gel, hydrothermal, co-precipitation, 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. The electrical poling of barium titanate provided the complete alignment of all the domains in the ceramic as in the single crystals. A review of recently published research papers allows us to conclude that the unique properties of ferroelectric nanoparticles offer an enormous range of applications, especially in material technologies, biology, and medicine.

REFERENCES

- [1] www.3dchem.com/inorganicmolecule.asp?id=1618
- [2] Ciftci, E., Rahaman, M.N., Shumsky, M., 2001. J. Mater. Sci., 36:4875.

- [3] Wang, L., Liu, L., Xue, D., Kang, H., Liu, C., 2007. *J. Alloys Comp.* 440:78.
- [4] Wada, S., Suzuki, T. and Noma, T., 1995. *J. Mater. Res.* 10:306.
- [5] Boulos, M., Guillemin-Fritsch, S., Mathieu, F., Durand, B., Lebey, T., Bley, V., 2005. *Solid State Ionics*,176:1301.
- [6] Cho, W.S., Hamada, E., 1998. *J. Alloys Comp.* 266:118
- [7] Goodman, G., 1986. ‘Ceramic Capacitor Materials’, in *Ceramic Materials for Electronics*. Ed. by R.C. Buchanan. Marcel Dekker, New York, pp.79–138.
- [8] W.-S.Cho, *J. Phys. Chem. Solids* (1998) 59:659.
- [9] W.-S. Cho, E. Hamada, *J. Alloys Comp.* (1998) 266:118
- [10] B. Li, X. Wang, L. Li, *Mater. Chem. Phys.* (2002) 78:292.
- [11] F. Guangneng, H. Lixia, H. Xueguang, *J. Cryst. Growth* (2005) 279:489.
- [12] H.S. Potdar, S.B. Deshpande, S.K. Date, *Mater. Chem. Phys.* (1999) 58:121.
- [13] L. Simon-Seveyrat, A. Hajjaji, Y. Emziane, B. Guiffard, D. Guyomar, *Ceram. Int.* (2007) 33:35.
- [14] A.V. Prasadarao, M. Suresh, S. Komarneni, *Materials Letters* (1999) 39:359.
- [15] Sonia, R.K. Patel, P. Kumar, C. Prakash, D.K. Agrawal, Low temperature synthesis and dielectric, ferroelectric and piezoelectric study of microwave sintered BaTiO₃ ceramics, *Ceramics International* (2012) 38:1585.
- [16] A.I. Ali, C.W. Ahn, Y.S. Kim, Enhancement of piezoelectric and ferroelectric properties of BaTiO₃ ceramics by aluminum doping, *Ceramics International* (In Press).
- [17] N.M., B.P. Zhang, W.G. Yang, D. Guo, Phase structure and nano-domain in high performance of BaTiO₃ piezoelectric ceramics, *Journal of the European Ceramic Society* (2012) 32:1059.
- [18] P. Zheng, J.L. Zhang, Y.Q. Tan, C.L. Wang, Grain-size effects on dielectric and piezoelectric properties of poled BaTiO₃ ceramics, *Acta Materialia*, (2012) 60:5022.
- [19] Hsieh, C.-L., Grange, R., Pu, Y. and Psaltis, D. Bioconjugation of barium titanate nano- crystals with immunoglobulin G antibody for second harmonic radiation imaging probes. *Biomaterials* (2010) 31:2272.
- [20] Hsieh, C.-L., Grange, R., Pu, Y. and Psaltis, D. (eds. Campagnola, P.J., Stelzer, E.H.K. and von Bally) *Proc. SPIE 7367, Advanced Microscopy Techniques, Munich, Germany* (2009) doi:10.1117/12.831506.
- [21] Hsieh, C.-L., Grange, R., Pu, Y. and Psaltis, D. Three-dimensional harmonic holographic microcopy using nanoparticles as probes for cell imaging. *Optics Express* (2009) 17:2880.