

Structure and Dielectric Properties of Perovskite
-Barium Titanate (BaTiO_3)

Hsiao-Lin, Wang

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Instructor: Prof. G. Selvaduray

San Jose State University

I. Introduction

The perovskite family includes many titanates used in various electroceramic applications, for example, electronic, electro-optical, and electromechanical applications of ceramics. Barium titanate, perovskite structure, is a common ferroelectric material with a high dielectric constant, widely utilized to manufacture electronic components such as multilayer capacitors (MLCs), PTC thermistors, piezoelectric transducers, and a variety of electro-optic devices^[1].

Because of people's demands, dielectric (essentially nonconducting) characteristics of ceramics materials are increasing rapidly. At the same time people are attempting to reduce the size of all communication devices as small and as light as possible. Due to this trend, high dielectric constant materials such as barium titanate nowadays become more and more important in ceramics materials.

This paper will describe perovskite structure, based on barium titanate composition, and interpret the theory of dielectric properties first. Then discuss how different compositions, additives, substitution, fabrication processes and defects that would influence BaTiO₃ based structure's dielectric properties. Last, briefly introduce the applications related to barium titanate dielectric properties such as multilayer ceramic capacitors (MLCs) and positive temperature coefficient (PTC) thermistors.

II. Structure of perovskite-Barium Titanate (BaTiO_3)

The perovskite-like structure, named after the CaTiO_3 perovskite mineral ^[2], is a ternary compound of formula ABO_3 that A and B cations differ in size. It is considered an FCC- derivative structure in which the larger A cation and oxygen together form an FCC lattice while the smaller B cation occupies the octahedral interstitial sites in the FCC array. There is only the oxygen being B cation's nearest neighbor.

The structure is a network of corner-linked oxygen octahedra, with the smaller cation filling the octahedral holes and the large cation filling the dodecahedral holes ^[3]. The unit cell of perovskite cubic structure is shown below in Figure 1.

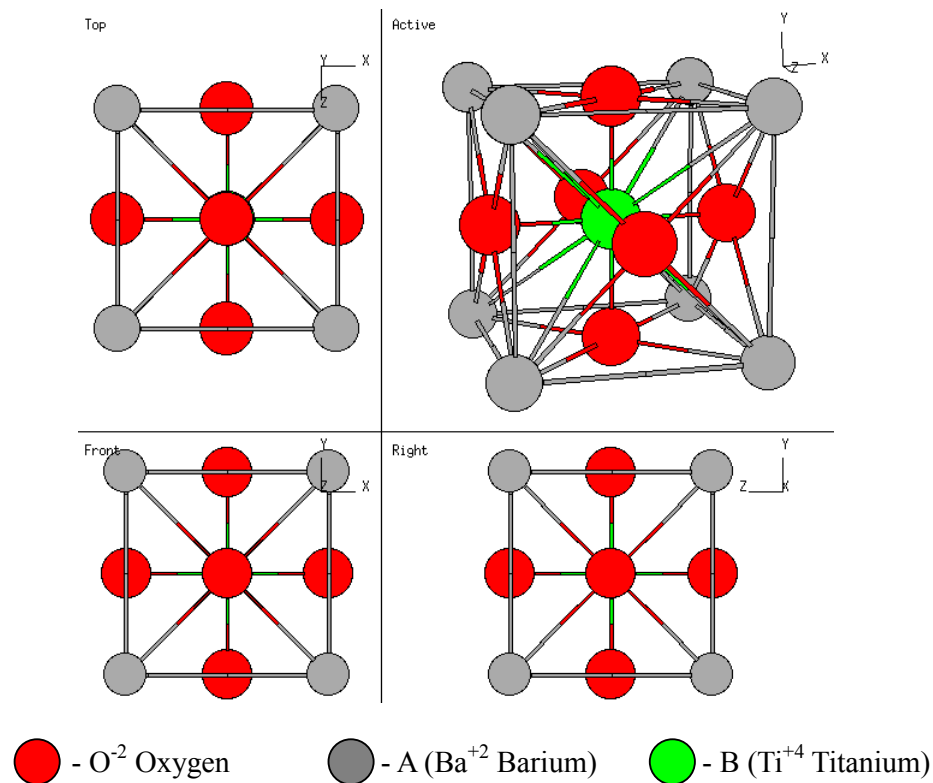


Figure 1. Perovskite Structure ^[4].

In Figure 1, we can see that the coordination number of A (Ba^{+2} Barium) is 12, while the coordination number of B (Ti^{+4} Titanium) is 6. In most cases, the above figure is somewhat idealized ^[6]. In fact, any structure consisting of the corner-linked oxygen octahedra with a small cation filling the octahedral hole and a large cation (if present) filling the dodecahedral hole is usually regarded as a perovskite, even if the oxygen octahedra are slightly distorted ^[6]. Also, it is unnecessary that the anion is oxygen. For example, fluoride, chloride, carbide, nitride, hydride and sulfide perovskites are also classified as the perovskite structures. As a result, we can say that perovskite structure has a wide range of substitution of cations A and B, as well as the anions, but remember that the principles of substitution must maintain charge balance and keep sizes within the range for particular coordination number. Because the variation of ionic size and small displacements of atoms that lead to the distortion of the structure and the reduction of symmetry have profound effects on physical properties, perovskite structure materials play such an important role in dielectric ceramic.

III. Principles of Dielectrics

Dielectrics and insulators can be defined as materials with high electrical resistivities ^[8]. A good dielectric is, of course, necessarily a good insulator, but the converse is by no means true ^[8]. Dielectric properties, dielectric constant, dielectric loss factor, dielectric resistivity, and dielectric strength will be interpreted as follow.

Capacitance. The principal characteristic of a capacitor is that an electrical charge Q can be stored ^[10]. The charge on a capacitor is given in Equation 1,

$$Q=CV \quad \text{Equation 1}$$

where V is the applied voltage and C is the capacitance ^[10]. The capacitance C contains both a geometrical and a material factor ^[10]. For a large plate capacitor of area A and thickness d the geometrical capacitance in vacuo is given by Equation 2

$$C_0=(A/d)*\epsilon_0 \quad \text{Equation 2}$$

where ϵ_0 is the permittivity (dielectric constant) of a vacuum ^[10]. If a ceramic material of permittivity ϵ' is inserted between the capacitor plates,

$$C=C_0*(\epsilon'/\epsilon_0)=C_0\kappa' \quad \text{Equation 3}$$

where κ' is the relative permittivity or relative dielectric constant, then the capacitance can be shown in Equation 3.. This is the material property that determines the capacitance of a circuit element.

Dielectric loss factor. The loss factor ϵ'' , as shown in Equation 4, is the primary criterion for the usefulness of a dielectric as an insulator material ^[11].

$$\epsilon''=\tan\delta/\epsilon' \quad \text{Equation 4}$$

In Equation 4, ϵ' is dielectric constant defined above, while $\tan\delta$ is the dissipation factor. For this purpose it is desirable to have a low dielectric constant and particularly a very small loss angle ^[11]. Applications that are desirable to obtain a high capacitor in the

smallest physical space, the high dielectric constant materials must be used and it is equally important to have a low value for the dissipation factor, $\tan\delta$ [11].

Dielectric strength. Dielectric strength is defined when the electric field is just sufficient to initiate breakdown of the dielectric [8]. It depends markedly on material homogeneity, specimen geometry, electrode shape and disposition, stress mode (DC, AC or pulsed) and ambient conditions [8].

IV. Dielectric Characteristics of Barium Titanate

Barium Titanate was the first developed piezoelectric ceramic and even now it is still widely used. It is also a well-known material used for capacitors. The crystallographic dimensions of the barium titanate lattice change with temperature, as shown in Figure 2, due to distortion of the TiO_6 octahedra as the temperature is lowered from the high temperature cubic form [2].

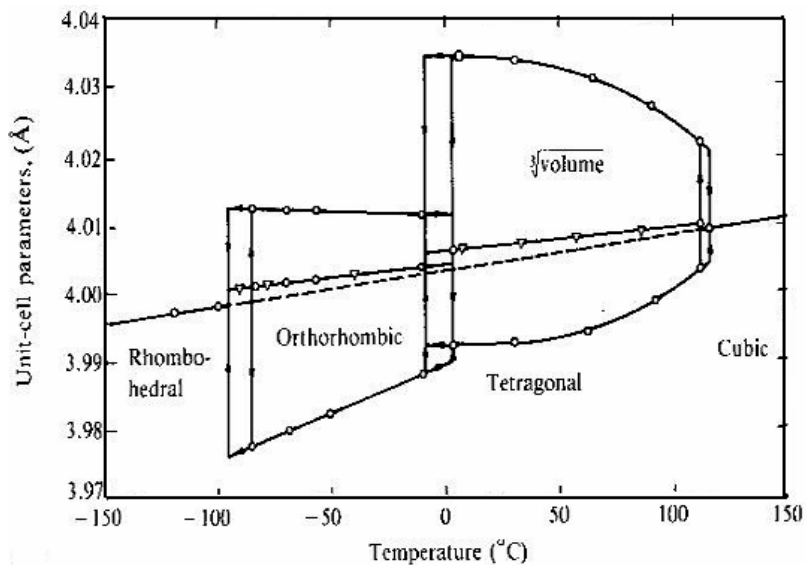


Figure 2. Lattice parameters of BaTiO_3 as a function of temperature [11].

Because the distorted octahedra are coupled together, there is a very large spontaneous polarization, giving rise to a large dielectric constant and large temperature dependence of the dielectric constant as shown in Figure 3 [11].

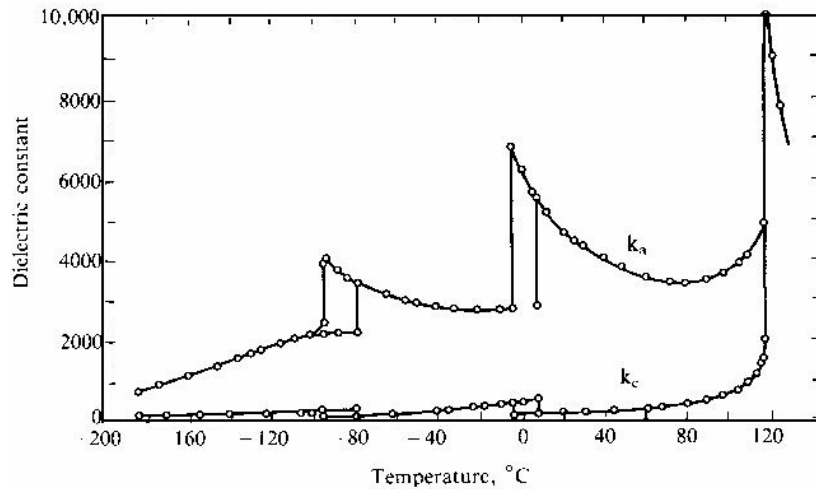


Figure 3. Dielectric constants of BaTiO₃ as a function of temperature [11].

In figure 2 we can see that above 120°C, Curie point T_c , barium titanate ceramic is cubic structure acting isotropic. The Ti atoms are all in equilibrium positions in the center of their octahedra [11]. Shifting of Ti atom due to applied electric fields could cause the structure to be altered, creating electric dipoles. For example, when temperature is below the Curie temperature, the octahedral structure changes from cubic to tetrahedral symmetry and the position of the titanium ion becomes an off-center position corresponding to a permanent electrical dipole. As the temperature is changed, the crystallographic dimensions change due to distortion of the octahedra resulting in

octahedra being coupled together and having a very large spontaneous polarization that leads to a large dielectric constant. These sensitive crystallographic fluctuations with the temperature are shown in Figure 4.

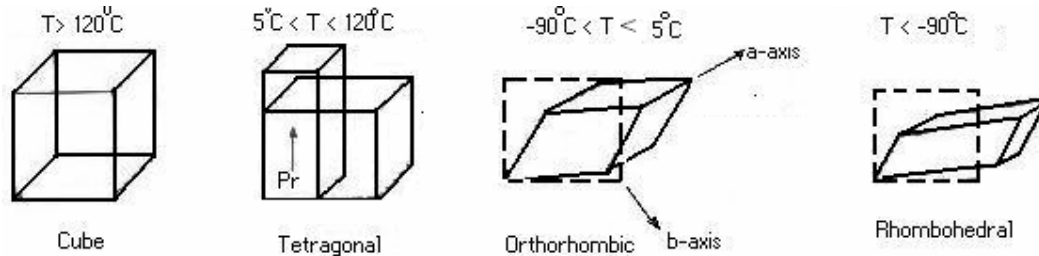


Figure 4. Crystallographic changes of BaTiO_3 [11].

The dielectric characteristics of barium titanate ceramics with respect to temperature, electric field strength, frequency and time (aging) are also very dependent on the substitution of minor amounts of other ions, on microstructure, and in particular on fine grain size. For example, the room-temperature relative dielectric constant increases as the grain size of the fast-fired BiTiO_3 ceramic is decreased [13]. When compared with milling method, chemical mixing techniques show an advantage in enhancing the microhomogeneity of additives, modifying the surface states and then have an effect on the properties of coated ceramics.

For instance, in coating process silica is a well-known sintering aid that improves the sintering behavior of BaTiO_3 particles and also can produce a core-shell-like structure. By adjusting the core-shell structure, we can control the dielectric properties. The

coating process not only can increase the shrinkage rate that improves the sintering behavior but also can inhibit the grain growth.

V. Applications

A. Multilayer ceramic capacitors (MLCs)-

Multilayer capacitors structure, as shown in Figure 5, enables the maximum capacitance available from a thin dielectric to be packed into the minimum space in a mechanically robust form ^[15].

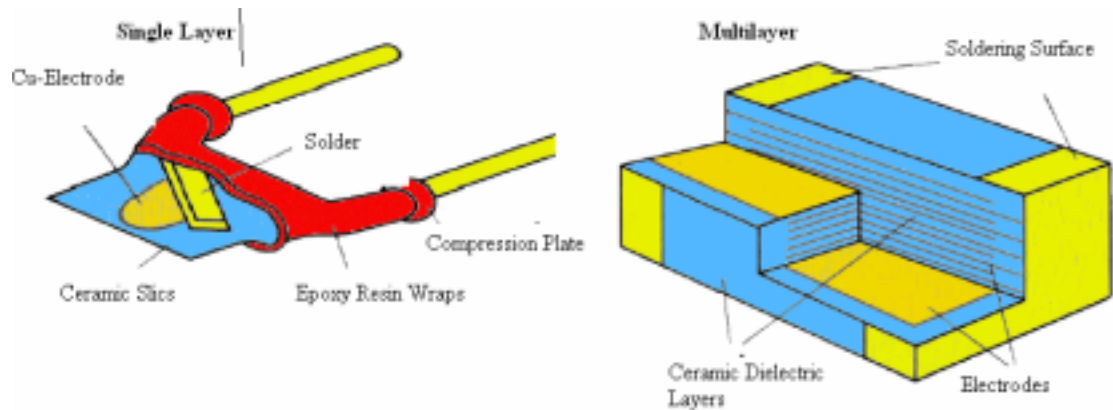


Figure 5. Schematic diagram of a multilayer ceramic capacitor construction ^[21].

Recently, multilayer ceramic capacitors (MLCs) with Ni electrodes have been increasingly produced to meet growing requirements for miniaturization, large capacitors and cost reduction ^[16]. Firing the dielectric materials in a low-oxygen partial pressure to prevent Ni from oxidizing is one method to miniaturize MLCs. Then addition of MgO and $\text{Li}_2\text{O-SiO}_2\text{-CaO}$ glass components are effective not only in preventing the dielectric

material from reducing and but also in controlling the temperature dependency of the dielectric constant. Because of appealing of heterogeneous microstructure, so-called core-shell structure that showed a typical ferroelectric domain pattern, microstructure controlling becomes extremely important to improve the reliability of MLCs within very thin dielectric layer thickness.

It was suggested that the microstructures and the electrical properties were influenced by the change of substitution modes of Mg and rare-earth oxide in perovskite [16]. For larger ion (La, Sm)-doped samples larger amount of MgO is necessary to suppress the grain growth and form the core-shell structure than smaller one (Dy, Ho, Er)-doped samples. Also, the solubility of rare-earth ions in BaTiO₃ has a linear relationship with the ionic radius. It is confirmed that the larger ion acting as donors mainly dissolves Ba site, while the smaller ion acting as both donors and acceptors dissolves both Ba- and Ti-sites. In recent years, MLCs with Ni internal electrodes composed of about 400 dielectric layers of below 2 μ m thickness have been developed [17].

B. Positive temperature coefficient (PTC) thermistors-

Positive temperature coefficient (PTC) materials prepared from doped semiconducting barium titanate ceramics can be used in various kind of electronic circuitry as a switching device or as a constant temperature heater [18]. In addition, PTC thermistors applications such as the measurement/detection/control of temperature or

parameters related to temperature are also important. These PTC materials are known to have a high temperature coefficient of resistance around Curie point and the ability of self-limiting, so they are as well come out to be a very useful device for sensor applications.

The positive temperature coefficient of resistance (PTCR) can be classified as critical temperature resistors because of the positive coefficient being associated with the ferroelectric Curie point. In fact, PTCR materials can be divided into four groups: polymer composites, ceramic composites, V_2O_3 compounds and $BaTiO_3$ -based compounds ($BaSrTi_3O$, $BaPbTiO_3\dots$) [19]. For $BaTiO_3$ -based compounds, $BaTiO_3$ is an insulator at room temperature. After doping with trivalent donors (e.g. La, Sb, Y) that substitute for the Ba^{+2} or with pentavalent donors (e.g. Sb, Nb, Ta) that substitute for Ti^{+4} , $BaTiO_3$ becomes semiconductive that shows a PTCR effect as shown in Figure 6.

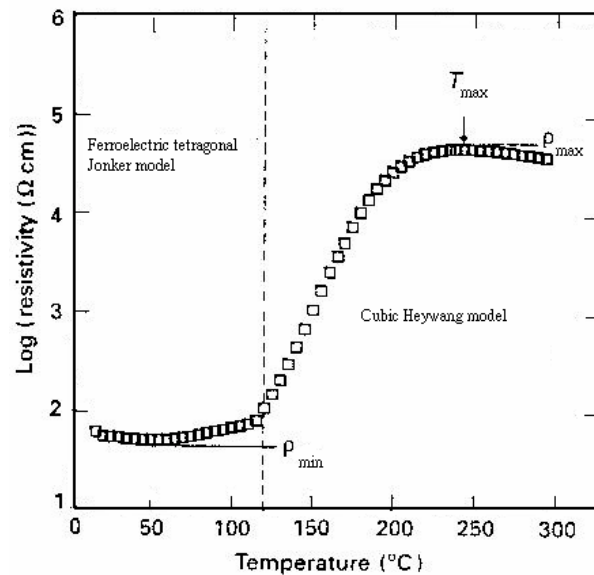


Figure 6. Typical resistivity behavior of a $BaTiO_3$ -type PTCR material [18].

PTCR applications can be classified in three main groups categorizing in Table 1.

Table 1. Classification of the PTCR applications [18].

Current limiters Using the attenuation of the current Fuses Using the attenuation rate of the current Colour TV and computer display degaussers Motor starters
Constant temperature heaters Using the I-V characteristic Mosquito killers Hair driers Heaters in trains and cars
Thermal sensors Using the R-T characteristic

VI. Summary and Conclusions

This paper discusses the structure of barium titanate perovskite based structure and some principles of dielectric properties. BaTiO₃ materials have been developed for dielectric applications for a long time that using various substitutional ions for Ba⁺² and Ti⁺⁴ to miniaturize the capacitors with large capacitance. These dielectric properties of barium titanate could be affected by many different parameters such as temperature, ambience, coating process, grain size, and etc. Because the crystallographic dimensions of BaTiO₃ are sensitive to temperature, we can see comprehensive applications of BaTiO₃ playing a significant role in dielectric materials.

VII. References

1. Wongduan Maison, Reinhard Kleeberg, Robert B. Heimann, and Sukon Phanichphant, *“Phase Content, Tetragonality, and Crystallite Size of Nanoscaled Barium Titanate Synthesized by The Catecholate Process: effect of calcinations temperature,”* Journal of the European Ceramic Society, **23**, 127-132 (2003).
2. L. L. Hench and L. K. West, Principles of Electronic Ceramics, (John Wiley & Sons, Inc., 1990), pp244-247.
3. Goldschmidt, V. M., *“Skifter Norske Videnskaps-Akad,”* Oslo, I: Mat. - Naturv. Kl., **2**, 8 (1926).
4. <http://cst-www.nrl.navy.mil/lattice/struk/perovskite.html>.
5. Bernard Jaffe, William R. Cook, Jr., and Hans Jaffe, Piezoelectric Ceramics, (Academic Press Limited, 1971), pp49-51.
6. *ibid*, p50.
7. A. J. Moulson and J. M. Herbert, Electroceramics, (Chapman and Hall, 1990), pp182-205.
8. *ibid*, pp182-184.
9. W. D. Kingery, H. K. Bowen, and D.R. Uhlmann, Introduction to Ceramics, 2nd ed. (John Wiley & Sons, New York), pp 913-973.
10. *ibid*, pp914-915.

11. W. D. Kingery, H. K. Bowen, and D.R. Uhlmann, op cit, pp926-927.
12. A. J. Moulson and J. M. Herbert, op cit, p243.
13. H. Mostaghaci and R. J. Brook, "*Microstructure Development and Dielectric Properties of Fast-Fired BaTiO₃ Ceramics,*" Journal of Materials Science, **21**, 3575-3580 (1986).
14. RenZheng Chen, AiLi Cui, XiaoHui Wang, ZhiLun Gui, and LongTu Li, "*Structure, Sintering Behavior and Dielectric Properties of Silica-Coated BaTiO₃,*" Materials Letters, **54**, 314-317 (2002).
15. A. J. Moulson and J. M. Herbert, op cit, p200.
16. Hiroshi Kishi, Noriyuki Kohzu, Junichi Sugino, Hitoshi Ohsato, Yoshiaki Iguchi and Takashi Okuda, "*The Effect of Rare-earth (La, Sm, Dy, Ho and Er) and Mg on the Microstructure in BaTiO₃,*" Journal of the European Ceramic Society, **19**, 1043-1046 (1990).
17. Hiroshi Kishi, Noriyuki Kohzu, Yoshiaki Iguchi, Junichi Sugino, Makoto Kato, Hitoshi Ohsato and Takashi Okuda, "*Occupational Sites and Dielectric properties of Rare-earth and Mn Substituted BaTiO₃,*" Journal of the European Ceramic Society, **21**, 1643-1647 (2001).
18. Suman Chatterjee and H. S. Maiti, "*A Novel Method of Doping PTC Thermistor Sensor Elements during Sintering through Diffusion by Vapour Phase,*" Materials

- Chemistry and Physics, **67**, 294-297 (2001).
19. B. Huybrechts, K. Ishizaki and M. Takata, “*Review The Positive Temperature Coefficient of Resistivity in Barium Titanate,*” Journal of Materials Science, **30**, 2463-2474 (1995).
20. Hiroshi Saito, Hirokazu Chazono, Hiroshi Kishi and Nobutatsu Yamaoka, “*X7R Multilayer Ceramic Capacitors with Nickel Electrode,*” Japanese Journal of applied physics, **30**, 2307-2310 (1991).
21. <http://www-iwe.etec.uni-karlsruhe.de/plainhtml/lehre/mad/pdf/md11.pdf>.