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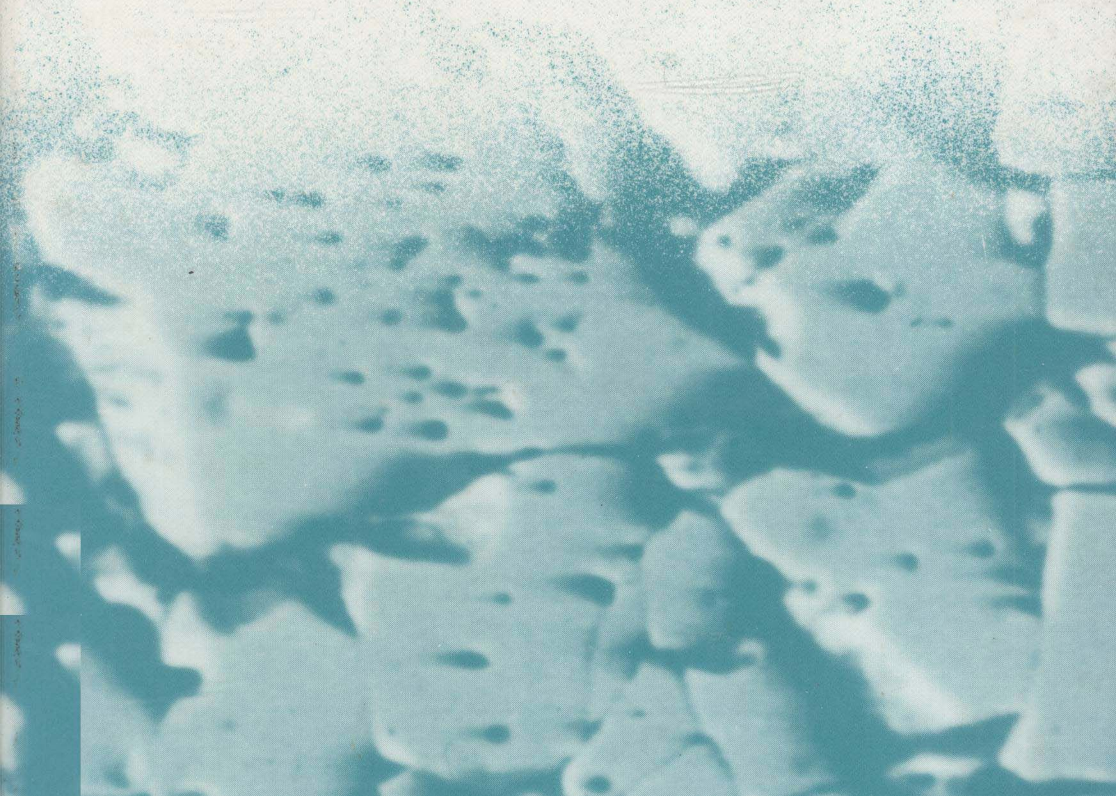
DIELECTRIC CERAMICS: PROCESSING, PROPERTIES, AND APPLICATIONS

K.M. Nair • J.P. Guha • A. Okamoto



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DIELECTRIC CERAMICS: PROCESSING, PROPERTIES, AND APPLICATIONS

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Preface

Since the discovery of ferroelectricity in barium titanate, extensive investigations of the dielectric and magnetic properties of inorganic ceramic materials and their solid solutions produced a variety of materials applicable to solid-state electronic devices. Among them, ceramic capacitative elements in electronic applications and electrical insulation in multilayer ceramic structures were the major areas where materials developments were needed to compete effectively against polymeric materials. Also, new applications and environmental restrictions demanded better material systems and processing conditions to provide improved reliability and better performance.

Today's global industrial markets need team efforts and strict materials management that encourage business leaders and researchers to work together. The American Ceramic Society is a main facilitator for new materials development and "on-time" manufacturing of quality materials through information transfer by bringing together management personnel and technical experts from diversified fields. During the last three years, the Society organized over ten international symposia in the area of electronics alone, and published the proceedings in the *Ceramic Transactions* series.

This volume is a collection of papers presented at the symposium on Dielectric Ceramics: Processing, Properties, and Applications, held during the Third International Ceramic Science and Technology Congress in San Francisco, CA, November 1-4, 1992. Over 20 invited papers and many contributed papers were presented during the three-day symposium. All of the papers included in this volume were reviewed through the Society's normal review process.

We, the editors, acknowledge and appreciate the contributions of the speakers, conference session chairs, manuscript reviewers, and Society officials for making this endeavor a successful one.

K.M. Nair
J.P. Guha
A. Okamoto

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STRUCTURE-PROPERTY RELATIONSHIPS IN HIGH PERMITTIVITY CERAMICS

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ABSTRACT

High dielectric constant ceramics are widely used today in electronic circuitry. In this paper, the mechanisms responsible for the high permittivity in ceramics capacitors are addressed and related to the temperature dependence of the permittivity and its modification. In addition, the structure-property relations controlling important corollary properties such as the dielectric loss, the electrical resistivity, and degradation in capacitors are also reviewed. Finally, the microstructure and crystal chemistry of some relaxor ferroelectrics are discussed.

INTRODUCTION

As the market in both technical and consumer electronics has grown, the production of high permittivity ceramic capacitors has burgeoned as well. While the technology for the preparation of capacitors has evolved over time (See Table 1), for the most part, the high dielectric constant materials used in large volume applications are still temperature-compensated $BaTiO_3$-based compositions. In this paper, the chemistry and crystal chemistry of these perovskite materials are discussed and related to the role of dopants in controlling the temperature dependence of the dielectric constant, domain wall motion, dielectric loss, and dc degradation. In addition, the structure, microstructure, and crystal chemistry of the lead-based relaxor ferroelectrics is reviewed.

Table 1: Capacitor Technology (From Reference 1).

Type of Ceramic Capacitor	**Thickness of the Dielectric Layer**	**Processing Technology**	**Grain Size of the Initial Powder**	**Production Process of the Powder**
Disk	100 to 1000 μm	Uniaxial Pressing	5 to 10 μm	Solid Routes
Old Multilayer	20 to 40 μm	Tape Casting	1 to 5 μm	95% Solid: 5% Wet
New Multilayer	10 to 20 μm	Wet Waterfall	1 to 2 μm	Wet Routes
Thin Films	1 to 5 μm	Chemical or Physical Deposition	0.1 to 0.5 μm	Sol-gel, vapor deposition

CHEMICAL AND CRYSTAL CHEMICAL CAUSES OF A HIGH DIELECTRIC CONSTANT

Ultimately, a high dielectric constant implies that an external electric field interacts strongly with the material in some way to polarize it. The net polarization in a material contains contributions from four mechanisms: electronic, ionic, dipolar, and space charge polarization. Of these, dipole polarization is the most attractive for the development of high permittivity materials with low dielectric loss in a low frequency range (< GHz). As can be seen in Fig. 1, there are ions, such as Ti^{4+}, Zr^{4+}, Nb^{5+}, and Ta^{5+}, which have electronic configurations near cross - over points in the energy levels for different orbitals. Such elements favor mixtures of orbital types and asymmetric coordination polyhedra. Thus, for Ti^{4+} the 3d, 4s and 4p orbitals of the Ti combine with the σ and π orbitals of its 6 neighbors to form molecular orbitals which favor distortion of the octahedron to a lower symmetry. Similarly, ions like Pb^{2+}, Bi^{3+} and Sb^{3+} adopt an electronic configuration in which the s^2 electrons form a region of negative charge on one side of the ion. In both cases, the asymmetry produces a local dipole which interacts strongly with an applied field, resulting in high relative dielectric constants, K, for PbO, and TiO_2. Not surprisingly, the ability to adopt deformed coordination polyhedra also promotes the displacement of one of the ions off a higher symmetry position in the crystal structure and ferroelectricity in these materials. Consequently, the ions shown in Fig. 1 are "active" ions which foster both high dielectric constants and ferroelectricity in oxide materials. As should be expected, the magnitude of the resultant spontaneous polarization is roughly proportional to the magnitude of the displacement[2] (See Figure 2).

Fig. 1: Active ions which promote hybrid bonds and ferroelectricity

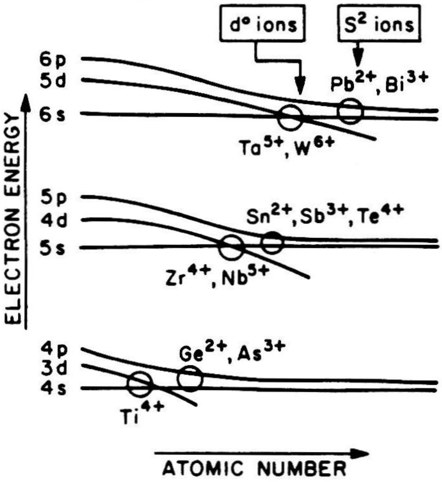
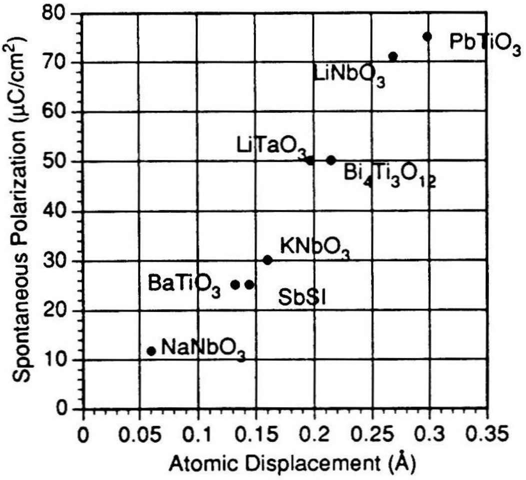


Fig. 2: Relation between the ionic displacement and the spontaneous polarization



The stability of the distorted coordination polyhedra characteristic of those adopted in a ferroelectric state is also apparent in aqueous solutions of active ions. Whereas ions such as Al^{3+} and Sn^{4+} form regular octahedral units with six H_2O molecules, both Ti^{4+} and Nb^{5+} form one short bond to an O^{2-} and five longer bonds to H_2O molecules[3]. This reduces the symmetry of the octahedra from m3m to 4mm. Given the tendency of active ions to form distorted coordinations in solution, it is not surprising that similar deformations in the near neighbor coordinations are favored in the ferroelectric state. It is interesting that Sn^{4+}, which is approximately the same size as Ti^{4+} and Nb^{5+}, but which has a different electronic configuration, does not show distorted octahedral arrangements either in aqueous solutions, or in perovskites like $BaSnO_3$ or $SrSnO_3$ [4].

For high dielectric constant capacitors, the most widely used ferroelectrics have the perovskite structure shown in Figure 3. Large 12 coordinated cations such as Ba, Sr, Pb and Ca occupy the cube corners in a cubic close-packed arrangement with the oxygens at the face centers. The smaller cation (such as Ti^{4+}, Zr^{4+}, Sn^{4+}, Nb^{5+}) is located near the center of the unit cell, coordinated with the neighboring oxygens, but displaced from the high symmetry position in the ferroelectric phase along <100>, <110>, or <111>, depending on both the material composition and the temperature. In $BaTiO_3$, the paraelectric/ferroelectric phase transition is characterized by displacement of the Ti and the O ions along [001]. With respect to the Ba lattice, the Ti ion moves 5 pm "up", the oxygens directly above and below the Ti 9 pm "down", and the "girdle" O around the Ti 6 pm "down." These displacements are related to an overdamped soft phonon. In $PbTiO_3$, however, the Ti and O ions shift in the same direction with respect to the lead lattice, with the Ti moving by 17 pm and the O by 47 pm. This motion corresponds to the soft mode motion observed by Raman spectroscopy[5].

Also shown in Figure 3 are the sigma and pi bonds present in the perovskite structure. The energy levels for the undistorted $[TiO_6]^{8-}$ octahedra are drawn in Figure 4, which depicts the relative stability of the σ and π bonds[3]. More complex diagrams are required for the lowered site symmetries resulting from ferroelectric displacements of the six coordinated cation.

Fig. 3: The prototype perovskite structure (a) Crystal structure (b) σ and π bonds

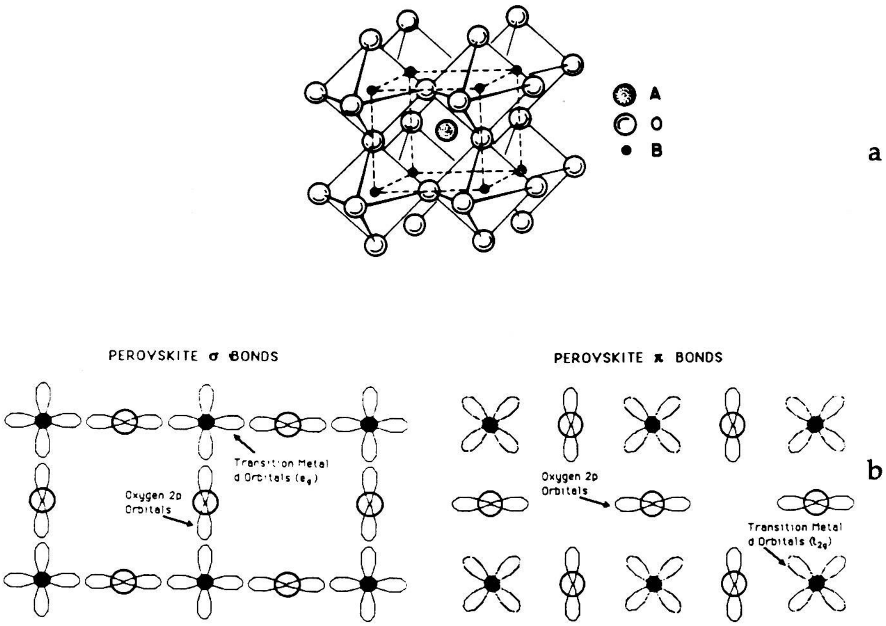
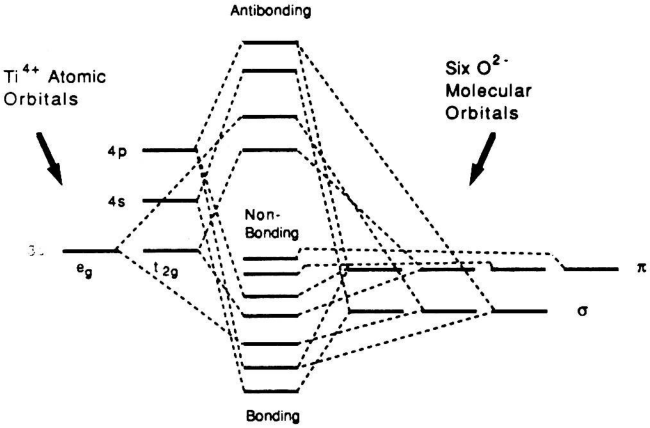


Fig. 4: Energy levels for σ and π bonds for TiO_6 octahedra



Phase transitions between any two of the distortions represent positions where the free energy of the phases are equal. Thus, near the phase transition temperatures, the coordination of the Ti can readily be distorted to either of the stable configurations. This strong interaction of the ionic displacement with an applied field is the basis of the high dielectric constant near the transition temperature. The presence of three ferroelectric transition temperatures in $BaTiO_3$ (as shown in Figure 5) is thus of tremendous technological importance as it provides high dielectric constant values over a 200°C temperature range.

For most applications, however, the strong temperature-dependence of the dielectric constant must be smoothed to eliminate unacceptable changes in circuit behavior under operating conditions. Unfortunately, however, flattening of the temperatures dependence of the dielectric constant is usually coupled to suppression of the maximum K value. Most often this is accomplished either by diluting the ferroelectric phase or by incorporating Curie point shifters and depressors. Table 2 lists typical compositions for three types of capacitors.

Fig. 5: Dielectric constant versus temperature for ceramic $BaTiO_3$ showing the three phase transitions (from reference 14)

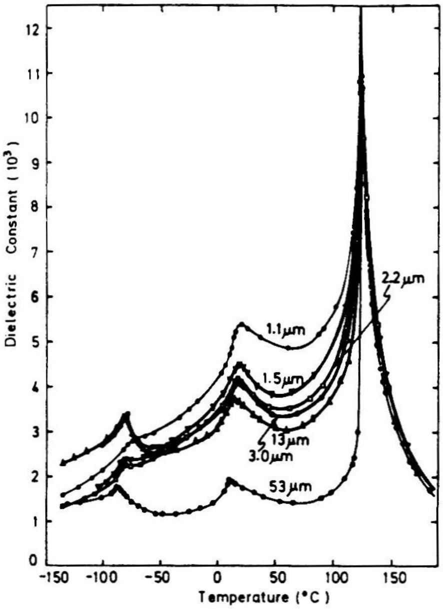


Table 2: Capacitor Compositions

Z5U: K = 5700 - 7000, tan δ < 0.03

$BaTiO_3$	84 - 90 wt %	Host
$CaZrO_3$	8 - 13 wt %	Shifter
$MgZrO_3$	0 - 3 wt %	Depressor
Dopants	1 - 3 wt %	Compensators and fluxes

X7R (BX): K = 1600 - 2000, tan δ < 0.025

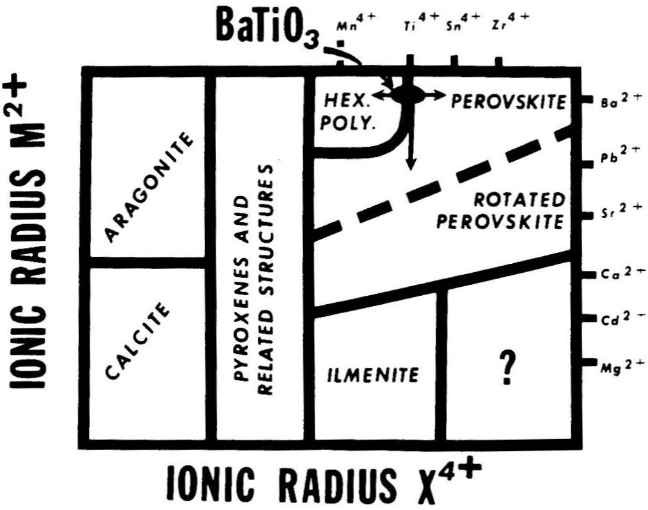
$BaTiO_3$	90 - 97 wt %	Host
$CaZrO_3$	2 - 5 wt %	Shifter
$BaCO_3$	0 - 5 wt %	Stoichiometry
Dopants	2 - 5 wt %	Compensators

NPO: K = 35, tan δ < 0.002

$BaTiO_3$	41 - 49 wt %	React to form other barium titanates
TiO_2	48 - 54 wt %	
Dopants	3 - 7 wt %	Compensators

The crystal chemical behavior of these dopant cations in $BaTiO_3$ is generally described by Figure 6, where a structure field map for ABO_3 materials is depicted. $BaTiO_3$ occupies a position along the border between the perovskite and the hexagonal polytypes phase fields[6]. Replacing Ba^{2+} with smaller cations such as Pb^{2+}, Ca^{2+}, and Sr^{2+} moves the material down into the perovskite and rotated perovskite regions. This is accompanied by shifts in the phase transition temperatures between different ferroelectric distortions. For the ferroelectric-paraelectric transition, addition of the active Pb^{2+} ion increases the Curie temperature linearly, because the lone pair of s electrons favors a tetragonal pyramid coordination as in PbO. Conversely, both Ca^{2+} and Sr^{2+} favor the undistorted cubic phase and lower the transition temperature, possibly because the smaller unit cell decreases the "rattling room" of the Ti ion. In all cases, the smaller divalent cations also reduce the two lower temperature phase transitions.

Fig. 6: Structure - Field Map for MXO_3 Materials



Substitution of larger or smaller cations for Ti, on the other hand, moves the material horizontally on the structure field map. As shown in Figure 7, for larger B site cations like Zr, this tends to pinch the three phase transitions together. Consequently, such materials display a single broad maximum in the dielectric constant as a function of temperature. Additional broadening of the dielectric maximum can be attributed to the presence of local compositional fluctuations in these materials. Smaller B cations, however, push the material into the hexagonal polytypes phase region. These structures can be regarded as a mixture of cubic and hexagonal close packing, where "stacking faults" in the original structure lead to some face sharing of the octahedra. In Figure 8, a comparison between cubic and hexagonal $BaTiO_3$ is shown. The hexagonal polytypes do not show pronounced ferroelectricity or high dielectric constants. It is possible, however, that the presence of a few stacking faults associated with polytypism might be useful in high K materials as a means to slow domain wall motion and reduce dielectric loss (see following section).

Fig. 7: Transition temperatures in $BaTiO_3$ as a function of Zr content

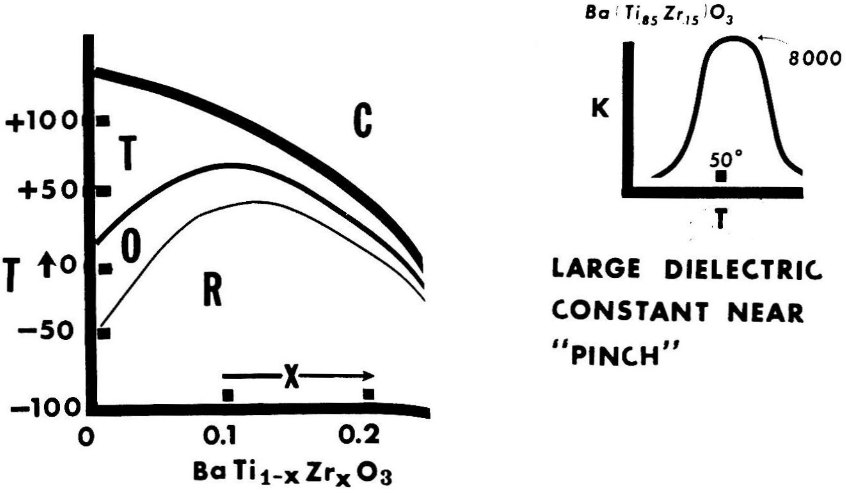


Fig. 8: Relation between cubic and hexagonal $BaTiO_3$