

Ferroelectric Ceramics: History and Technology

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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 capacitors. Since that time, they have been the heart and soul of several multibillion dollar industries, ranging from high-dielectric-constant capacitors to later developments in piezoelectric transducers, positive temperature coefficient devices, and electrooptic light valves. Materials based on two compositional systems, barium titanate and lead zirconate titanate, have dominated the field throughout their history. The more recent developments in the field of ferroelectric ceramics, such as medical ultrasonic composites, high-displacement piezoelectric actuators (Moonies, RAINBOWS), photostrictors, and thin and thick films for piezoelectric and integrated-circuit applications have served to keep the industry young amidst its growing maturity. Various ceramic formulations, their form (bulk, films), fabrication, function (properties), and future are described in relation to their ferroelectric nature and specific areas of application.

I. Introduction

SINCE the discovery of ferroelectricity in single-crystal materials (Rochelle salt) in 1921 and its subsequent extension into the realm of polycrystalline ceramics (barium titanate, BaTiO_3) during the early to mid-1940s, there has been a continuous succession of new materials and technology developments that have led to a significant number of industrial and commercial applications that can be directly credited to this most unusual phenomenon. Among these applications are high-dielectric-constant capacitors, piezoelectric sonar and ultra-

sonic transducers, radio and communication filters, pyroelectric security surveillance devices, medical diagnostic transducers, stereo tweeters, buzzers, gas ignitors, positive temperature coefficient (PTC) sensors and switches, ultrasonic motors, electrooptic light valves, thin-film capacitors, and ferroelectric thin-film memories.

The history of the discovery of ferroelectricity (electrically switchable spontaneous polarization) is a fascinating one that extends as far back as the mid-1600s when Rochelle salt (sodium potassium tartrate tetrahydrate) was first prepared by Elie Seignette in La Rochelle, France, for medicinal purposes. However, it was approximately 200 years later before this water-soluble, crystalline material would be investigated for its pyroelectric (thermal-polar) properties, another half century before its piezoelectric (stress-polar) properties would be uncovered, and finally another 40 years would pass before ferroelectricity (a hypothetical but yet unproved property of solids at the turn of the 20th century) would be first discovered by Joseph Valasek in this same material.¹ Rochelle salt was a popular material in these initial studies, because it was readily available and easily grown as large single crystals of excellent optical quality, but its water solubility eventually led to its disuse in later years. Several excellent papers on the history of ferroelectricity have been written, and the reader is referred to these for many of the details.²⁻⁶

This paper is intended to cover only the highlights of ferroelectric ceramics and cannot hope to treat all of its diverse aspects. In this regard, only personalities and companies involved in the early history are specifically mentioned, although it is clearly recognized that, since then, there have been many excellent individuals and institutions that have been involved in the research, development, and application of these very interesting materials.

(1) Chronological History of Ferroelectric Materials

A chronological listing of many of the more notable specific events in the history of ferroelectric materials is given in Table I. Because this article emphasizes a comprehensive review of ferroelectric (FE) polycrystalline ceramics from a materials point of view, timeline events involving compositions, processing, fabrication techniques, properties, patents, and applications are all included in Table I, whereas the specifics involving ferroelectric single crystals and the development of the phenomenological basis for the ferroelectric phenomenon are

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Table I. Notable Events in the History of Ferroelectric Materials

Timeline	Event [†]
1824	Pyroelectricity discovered in Rochelle salt
1880	Piezoelectricity discovered in Rochelle salt, quartz, and other minerals
1912	Ferroelectricity first proposed as property of solids
1921	Ferroelectricity discovered in Rochelle salt
1935	Ferroelectricity discovered in KH ₂ PO ₄
1941	BaTiO ₃ high- <i>K</i> (>1200) capacitors developed
1944	Ferroelectricity discovered in ABO ₃ -type perovskite BaTiO ₃
1945	BaTiO ₃ reported as useful piezo transducer, Pat. No. 2 486 560
1949	Phenomenological theory of BaTiO ₃ introduced
1949	LiNbO ₃ and LiTaO ₃ reported as FE
1951	Concept of antiferroelectricity introduced
1952	PZT reported as FE solid-solution system, phase diagram established
1953	PbNb ₂ O ₆ reported as FE
1954	PZT reported as useful piezo transducer, Pat. No. 2 708 244
1955	PTC effect in BaTiO ₃ reported
1955	Chemical coprecipitation of FE materials introduced
1955	Alkali niobates reported as FE
1957	BaTiO ₃ barrier layer capacitors developed
1959	PZT 5A and 5H MPB-type piezo compositions, Pat. No. 2 911 370
1961	Lattice dynamics theory for FE materials, soft modes introduced
1961	PMN relaxor materials reported
1964	Oxygen/atmosphere sintering for FEs developed
1964	FE semiconductor (PTC) devices developed
1967	Optical and E/O properties of hot-pressed FE ceramics reported
1969	Terms “ferroic” and “ferroelasticity” introduced
1969	Optical transparency achieved in hot-pressed PLZT ceramics
1970	PLZT compositional phase diagram established, Pat. No. 3 666 666
1971	Useful E/O properties reported for PLZT, Pat. No. 3 737 211
1973	Oxygen/atmosphere sintering of PLZT to full transparency
1977	FE thin films developed
1978	Engineered (connectivity designed) FE composites developed
1980	Electrostrictive relaxor PMN devices developed, Pat. No. 5 345 139
1981	Sol-gel techniques developed for the preparation of FE films
1983	Photostrictive effects reported in PZT and PLZT
1991	Moonie piezo flextensional devices developed, Pat. No. 4 999 819
1992	RAINBOW piezo bending actuators developed, Pat. No. 5 471 721
1993	Integration of FE films to silicon technology, Pat. No. 5 038 323
1997	Relaxor single-crystal materials developed for piezo transducers

[†]FE is ferroelectric, *K* is relative dielectric constant, PZT is lead zirconate titanate, MPB is morphotropic phase boundary, PLZT is lead lanthanum zirconate titanate, PMN is lead magnesium niobate, PTC is positive temperature coefficient, E/O is electrooptic, RAINBOW is reduced and internally biased oxide wafer.

not treated in detail. The time period is from the early 1800s to the present (1999), involving events from the early work on single-crystal Rochelle salt to (1) the birth of ferroelectric ceramics in the 1940s, (2) the development of lead zirconate titanate (PZT) piezoelectric ceramics in the mid-1950s, (3) the

research and development of transparent electrooptic lead lanthanum zirconate titanate (PLZT) ceramics the late 1960s, (4) the engineered ferroelectric composites of the late 1970s, (5) the development of lead magnesium niobate (PMN) relaxor ceramics and the use of sol-gel techniques for the preparation of ferroelectric films in the 1980s, (6) the strain-amplified actuators of the early 1990s, and (7) the current integrated ferroelectric films on silicon. Many of the items listed in Table I are described in detail in separate sections throughout the paper.

(2) Birth of Ferroelectric Ceramics

The story of the discovery of ferroelectricity and piezoelectricity in ceramic materials is equally fascinating and began in the early 1940s under a cloud of secrecy, because World War II was under way. Spurred on by the pressing need for higher-dielectric-constant capacitors than could be obtained from stearite, mica, TiO₂, MgTiO₃, and CaTiO₃ (*K* ≤ 100), unpublished work by Thurnauer⁷ and Wainer and Solomon⁸ firmly established BaTiO₃ as a new type of ceramic capacitor with *K* > 1100. Near the end of World War II, in the mid-1940s, publications began to appear in the open literature, and it became evident that concurrent work on BaTiO₃ as a high-dielectric-constant material had been conducted by several countries, including the United States, United Kingdom, USSR, and Japan. Shortly thereafter, in 1945 and 1946, the work of Wul and Goldman⁹ in the USSR and von Hippel's group¹⁰ at the Massachusetts Institute of Technology established that the source of the high dielectric constant in BaTiO₃ emanated from its ferroelectric properties. Work on single-crystal BaTiO₃ subsequently corroborated these findings.

The knowledge of the ferroelectric nature of ceramic BaTiO₃ proved to be invaluable when it was discovered by Gray¹¹ (in 1945) that an external electric field could orient the domains within the grains, thus producing a ceramic material that acted very similar to a single crystal possessing both ferroelectric and piezoelectric properties. This electrical aligning, or “poling” process as it has come to be called, was thus correctly identified as the key to turning an inert ceramic into an electromechanically active material with a multitude of industrial and commercial uses. This was a most startling discovery, because the prevailing opinion was that ceramics could not be piezoelectrically active, because the sintered and randomly oriented crystallites would, on the whole, cancel out each other. This

Abbreviations Used

Ferroelectric Materials

PZT	Lead zirconate titanate
PLZT	Lead lanthanum zirconate titanate
PMN	Lead magnesium niobate
PT	Lead titanate
PZN	Lead zinc niobate
PSZT	Lead stannate zirconate titanate
PZ	Lead zirconate
BST	Barium strontium titanate
SBT	Strontium bismuth titanate

Others

FE	Ferroelectric
AFE	Antiferroelectric
PE	Paraelectric
SFE	Slim-loop ferroelectric
PTC	Positive temperature coefficient
NTC	Negative temperature coefficient
MLC	Multilayer capacitor
BLC	Barrier layer capacitor
MPB	Morphotropic phase boundary

proved not to be the case for ferroelectric crystallites, because they could be permanently aligned or reoriented in an electric field, somewhat analogous to magnetic alignment in permanent magnets.

Thus, as pointed out by Jaffe¹² in his excellent treatise on piezoelectric ceramics, the three fundamental steps that were critical to the understanding of ferroelectricity and piezoelectricity in ceramics were (1) the discovery of the unusually high dielectric constant of BaTiO₃, (2) the discovery that the origin of the high dielectric constant was due to its ferroelectric (permanent internal dipole moment) nature, thus ushering in a new class of ferroelectrics (the simple oxygen octahedral ABO₃ group), and (3) the discovery of the electrical poling process that aligns the internal dipoles of the crystallites (domains) within the ceramic and causes it to act very similar to a single crystal. For more details on the history of ferroelectric ceramics, the reader is referred to several excellent publications.^{13–15}

(3) Basis for Piezoelectricity in Solids

Piezoelectricity, a property possessed by a select group of materials, was discovered in 1880 by Jacques and Pierre Curie during their systematic study of the effect of pressure on the generation of electrical charge by crystals, such as quartz, zincblende, and tourmaline. The name “piezo” is derived from the Greek, meaning “to press;” hence, piezoelectricity is the generation of electricity as a result of a mechanical pressure. Cady¹⁶ 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.”

An understanding of the concept of piezoelectricity in solids begins with an understanding of the internal structure of the material; for purposes here, consider a single crystallite. This crystallite has a definite chemical composition and, hence, is made up of ions (atoms with positive or negative charge) that are constrained to occupy positions in a specific repeating relationship to each other, thus building up the structure or lattice of the crystal. The smallest repeating unit of the lattice is called the unit cell, and the specific symmetry possessed by the unit cell determines whether it is possible for piezoelectricity to exist in the crystal. Furthermore, the symmetry of a crystal's internal structure is reflected in the symmetry of its external properties (Neumann's principle).¹⁶

The elements of symmetry that are utilized by crystallographers to define symmetry about a point in space, e.g., the central point of a unit cell, are (1) a center of symmetry, (2) axes of rotation, (3) mirror planes, and (4) combinations of these. All crystals can be divided into 32 different classes or point groups utilizing these symmetry elements, as shown in Fig. 1. These 32 point groups are subdivisions of seven basic crystal systems that are, in order of ascending symmetry, triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral (trigonal), hexagonal, and cubic. Of the 32 point groups, 21 classes are noncentrosymmetric (a necessary condition for piezoelectricity to exist) and 20 of these are piezoelectric. One class, although lacking a center of symmetry, is not piezoelectric because of other combined symmetry elements. A lack of a center of symmetry is all-important for the presence of piezoelectricity when one considers that a homogeneous stress is centrosymmetric and cannot produce an unsymmetric result, such as a vector-quantity-like polarization, unless the material lacks a center of symmetry, whereby a net movement of the positive and negative ions with respect to each other (as a result of the stress) produces electric dipoles, i.e., polarization. Furthermore, for those materials that are piezoelectric but not ferroelectric (i.e., they do not possess spontaneous polarization), the stress itself is the only means by which the dipoles are generated. For piezoelectricity, the effect is linear and reversible, and the magnitude of the polarization is dependent on the magnitude of the stress and the sign of the charge produced is dependent on the type of stress (tensile or compressive).

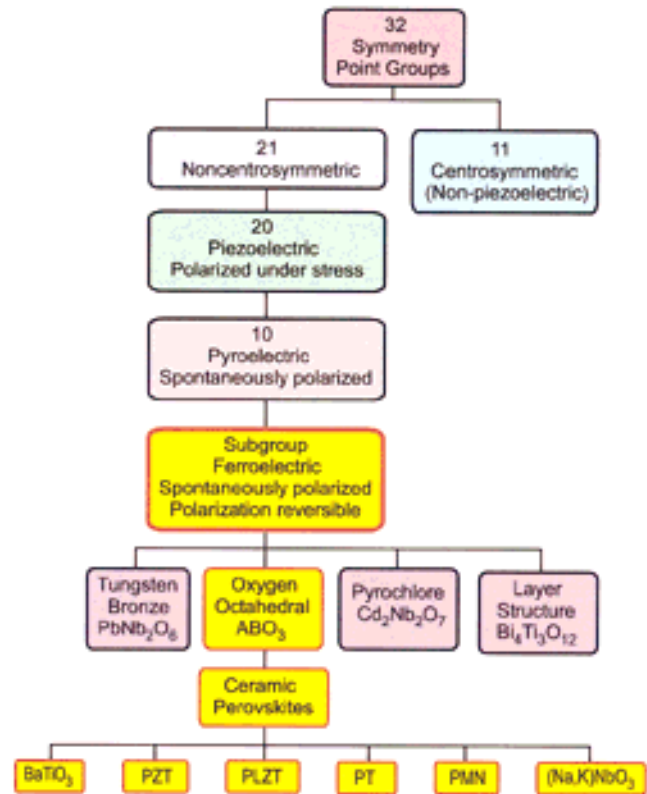


Fig. 1. Interrelationship of piezoelectric and subgroups on the basis of symmetry.

(4) Piezoelectricity in Ferroelectric Ceramics

As mentioned previously, the poling process is the critical element in being able to utilize the piezoelectric effect in a ferroelectric ceramic. Without poling, the ceramic is inactive, even though each one of the individual crystallites is piezoelectric itself. With poling, however, the ceramic becomes extremely useful, provided that it is not heated above its Curie temperature (T_C), where it loses its polarization and all of the orientation of the polarization produced by the poling process.¹⁷

Two effects are operative in piezoelectric crystals, in general, and in ferroelectric ceramics, in particular. The direct effect (designated 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 electrical field. Both of these effects are illustrated in Fig. 2 as cartoons for easy grasp of the principles.

The basic equations that describe these two effects in regard to electric and elastic properties are¹³

$$D = dE + \varepsilon^T E \quad (\text{generator}) \quad (1)$$

$$S = s^E T + dE \quad (\text{motor}) \quad (2)$$

where D is the dielectric displacement (consider it equal to polarization), T the stress, E the electric field, S the strain, d a piezoelectric coefficient, s the material compliance (inverse of modulus of elasticity), and ε the dielectric constant (permittivity). The superscripts indicate a quantity held constant: in the case of ε^T , the stress is held constant, which means that the piezoelectric element is mechanically unconstrained, and, in the case of s^E , the electric field is held constant, which means the electrodes on the element are shorted together. Equations (1) and (2), in matrix form, actually describe a set of equations that relate these properties along different orientations of the material. Because of the detailed nature of the many equations

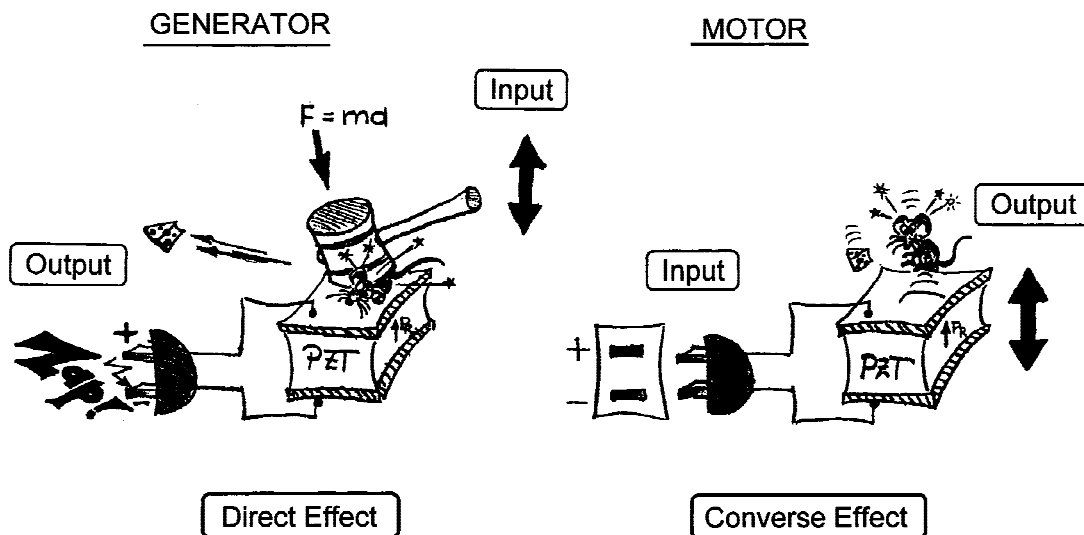


Fig. 2. Piezoelectric effects in ferroelectric ceramics.

involved, the reader is referred to several sources on the subject.^{13,18–20} Suffice it to say that, because this is a piezoelectric solid, Eqs. (1) and (2) relate given properties, such as electric displacement (polarization) and strain to both the mechanical and electrical states of the material. Furthermore, these properties are directional quantities, and, hence, they are usually specified with subscripts to identify the conditions under which they are determined, e.g., d_{31} indicates that this piezoelectric coefficient relates to the generation of polarization (direct effect) in the electrodes perpendicular to the 3 or vertical direction and to the stress mechanically applied in the 1 or lateral direction; d_{33} indicates the polarization generated in the 3 direction when the stress is applied in the 3 direction. Typical relationships for this coefficient are:

$$D_3 = d_{33}T_3 \quad (\text{direct effect}) \quad (3)$$

$$S_3 = d_{33}E_3 \quad (\text{converse effect}) \quad (4)$$

where the d coefficients are numerically equal in both equations. 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. High d coefficients are desirable for those materials that are utilized in motional or vibrational devices, such as sonar and sounders.

In addition to the d coefficients, open-circuit g coefficients are also used to evaluate piezoelectric ceramics for their ability to generate large amounts of voltage per unit of input stress. The g constant is related to the d constant via the relationship

$$g = \frac{d}{K\epsilon_0} \quad (5)$$

where K is the relative dielectric constant and ϵ_0 the permittivity of free space (8.854×10^{-12} F/m). Thus, a high g constant is possible for a given d coefficient if the material has a low K . High- g -constant ceramics are usually ferroelectrically hard materials that do not switch their polarization readily and possess lower K values. They are used in devices such as portable gas ignitors and patio lighters.

The piezoelectric coupling factor (e.g., k_{33} , k_{31} , and k_p) is a convenient and direct measurement of the overall strength of the electromechanical effect, i.e., the ability of the ceramic transducer to convert one form of energy to another. It is defined as the square root of the ratio of energy output in electrical form to the total mechanical energy input (direct effect), or the square root of the ratio of the energy available in mechanical form to the total electrical energy input (converse effect). Because the conversion of electrical to mechanical en-

ergy (or vice versa) is always incomplete, k is always less than unity. Commonly used as a figure-of-merit for piezoelectrics, the higher k values are most desirable and constantly sought after in new materials. For ceramics, k_p is a typical measurement used in comparing materials—values ranging from 0.35 for BaTiO₃ to as high as 0.72 for PLZT.

All of the properties mentioned here may be realized in a piezoelectric ceramic, which is, in reality, a poled ferroelectric ceramic material. During the process of poling, there is a small expansion of the material along the poling axis and a slight contraction in both directions perpendicular to it. The strength of the poling field, often in combination with elevated temperature, is an important factor in determining the extent of alignment and, hence, the resulting properties. Alignment is never complete; however, depending on the type of crystal structure involved, the thoroughness of poling can be quite high, ranging from 83% for the tetragonal phase to 86% for the rhombohedral phase, and to 91% for the orthorhombic phase, when compared with single-domain, single-crystal values. Because all ceramic bodies are macroscopically isotropic in the "as-sintered" condition and must be poled to render them useful as piezoelectric materials, they are all ferroelectric as well as piezoelectric.

(5) Basis for Ferroelectricity in Ceramics

Figure 1 shows that there are 10 crystal classes out of a possible 20 that are designated as pyroelectric. This group of materials possesses the unusual characteristic of being permanently polarized within a given temperature range. Unlike the more general piezoelectric classes that produce a polarization under stress, the pyroelectrics develop this polarization spontaneously and form permanent dipoles in the structure. This polarization also changes with temperature—hence, the term pyroelectricity. Pyroelectric crystals, such as tourmaline and wurtzite, are often called polar materials, thus referring to the unique polar axis existing within the lattice. The total dipole moment varies with temperature, leading to a change in sign for the current flowing out of a short-circuited crystal.

A subgroup of the spontaneously polarized pyroelectrics is a very special category of materials known as ferroelectrics. Similar to pyroelectrics, materials in this group possess spontaneous dipoles; however, unlike pyroelectrics, these dipoles are reversible by an electric field of some magnitude less than the dielectric breakdown of the material itself. Thus, the two conditions necessary in a material to classify it as a ferroelectric are (1) the existence of spontaneous polarization and (2) a demonstrated reorienting of the polarization.

Four types of ceramic ferroelectrics are also given in Fig. 1

as subcategories of the general group of ferroelectric materials, with typical examples representing the type based on its unit-cell structure: (1) the tungsten-bronze group, (2) the oxygen octahedral group, (3) the pyrochlore group, and (4) the bismuth layer-structure group. Of these, the second group (ABO_3 perovskite type) is by far the most important category, economically. The families of compositions listed (BaTiO_3 , PZT, PLZT, PT (lead titanate), PMN, and $(\text{Na,K})\text{NbO}_3$) represent the bulk of the ferroelectric ceramics manufactured in the world today.

A typical ABO_3 unit-cell structure is given in Fig. 3. For example, the PLZT unit cell consists of a corner-linked network of oxygen octahedra with Zr^{4+} and Ti^{4+} ions occupying sites (B sites) within the octahedral cage and the Pb^{2+} and La^{3+} ions situated in the interstices (A sites) created by the linked octahedra. As a result of the different valency between Pb^{2+} and La^{3+} , some of the A sites and B sites are vacant (referred to as vacancies) to maintain electrical neutrality in the structure.

When an electric field is applied to this unit cell, the Ti^{4+} or Zr^{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, it is most often the case that an individual ionic movement only closely approximates an alignment with the electric field. However, when this ionic movement does occur, it leads to a macroscopic change in the dimensions of the unit cell and the ceramic as a whole. The dimensional change can be as large as a few tenths of a percent elongation in the direction of the field and approximately one-half that amount in the other two orthogonal directions. The original random orientation of the domain polarization vectors (virgin condition) can be restored by heating the material above its T_C . This process is known as thermal depoling.

Also shown in Fig. 3 is the reversibility of the polarization caused by the displacement of the central Ti^{4+} or Zr^{4+} ion. Displacement is illustrated here as occurring along the c axis in

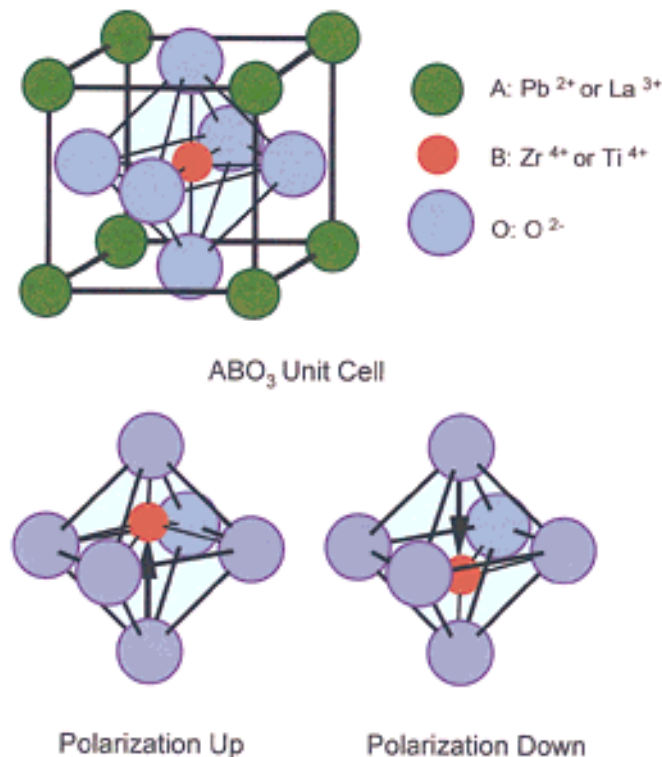


Fig. 3. Perovskite ABO_3 unit cell for PZT or PLZT, illustrating 180° polarization reversal for two of the six possible polarization states produced by displacement of the central cation in the tetragonal plane.

a tetragonal structure, although it should be understood that it can also occur along the orthogonal a or b axes as well. The views of “polarization up” and “polarization down” (representing 180° polarization reversal) show two of the six possible permanent polarization positions.

When many of these unit cells, which are adjacent to each other, switch in like manner, this is referred to as domain reorientation or switching. The homogeneous areas of the material with the same polarization orientation are referred to as domains, with domain walls existing between areas of unlike polarization orientation. There exists in tetragonal materials both 90° (strain-producing domains on switching) and 180° domains (nonstrain-producing domains), whereas the strain-producing entities in rhombohedral materials are 71° and 109° domains with the 180° domains remaining as nonstrain producing. Macroscopic changes occur in the dimensions of the material when strain-producing domains are switched.

Because of the empirical nature of determining the reversibility of the dipoles (as detected by a hysteresis loop measurement), one cannot predict the existence of ferroelectricity in a new material with much accuracy. However, the basis for the existence of ferroelectricity rests primarily on structural and symmetry considerations. The special relationship of ferroelectrics as a subgroup of piezoelectrics (Fig. 1) infers that “all ferroelectrics (poled) are piezoelectric, but not all piezoelectrics are ferroelectric.” The current number of ferroelectrics is in the thousands when one includes the many ceramic solid-solution compositions. Ferroelectrics are no longer the great “accident of nature” that they were once thought to be in the 1920s and 1930s.

(6) Electrostriction in Ferroelectric Ceramics

Electrostriction is another electromechanical effect that exists in ferroelectric ceramics. In electrostriction, the sign of the deformation that occurs with an electric field is independent of the polarity of the field and is proportional to even powers of the field. In piezoelectricity, the deformation is linear with respect to the applied field and changes sign when the field is reversed. This means in practical terms that electrostriction produces an expansion in most materials in the direction of the field regardless of its polarity, and this expansion relaxes back to zero when the field is removed. The corresponding equations are

$$S = mE^2 \quad (\text{in terms of electric field}) \quad (6)$$

$$S = QP^2 \quad (\text{in terms of polarization}) \quad (7)$$

where P is the polarization and m and Q the corresponding electrostrictive coefficients. Similar to piezoelectricity, electrostriction deals with vector quantities, and, hence, appropriate subscripts must be used.

Although electrostriction is a general property of all dielectric materials, whether they are crystalline, amorphous, polar, or centrosymmetric, it can be particularly large in ferroelectric materials just above their T_C , where an electric field can enforce the energetically unstable ferroelectric phase. More commonly, this effect is utilized to good advantage in relaxor materials, such as PMN, PZN (lead zinc niobate), and PLZT, where the T_C is not sharp but rather is spread out over a moderate temperature range, thus allowing for a reasonable temperature range of operation for devices made from them.

Electrostrictive materials can be operated either in the electrostrictive mode (as stated above) or in the field-biased piezoelectric mode. In the latter case, a dc electric field bias is applied to the material to induce a ferroelectric polarization, whereupon the material acts as a normal piezoelectric as long as the field is applied, and, the stronger the field, the higher the piezoelectric effect until saturation sets in. The relationships relating the resulting piezoelectric d coefficient to the induced polarization and the dielectric permittivity are

$$d_{33} = 2Q_{11}P_3\epsilon_{33} \quad (8)$$

$$d_{31} = 2Q_{12}P_3\epsilon_{33} \quad (9)$$

where Q_{11} and Q_{12} are the longitudinal and transverse electrostrictive coefficients, respectively. Thus, a large dielectric constant and a high polarization are required to produce a large induced piezoelectric coefficient. These Q coefficients are essentially independent of temperature.^{21–24}

Some advantages for electrostrictors over conventional piezoelectrics are (1) hysteresis in the strain-field dependence is minimal or negligible in a selected temperature range, (2) realized deformation is more stable and comparable to the best piezoelectric ceramics, and (3) no poling is required. These advantages, however, are balanced by the disadvantages of (1) a limited usable temperature range due to the strong temperature dependence of the electrostrictive effect and (2) especially small deformation at low fields, because electrostriction is very nearly a quadratic function at low electric fields, which then usually necessitates higher operating voltages to achieve moderate deflection.

Although the actual mechanism or mechanisms leading to the large electrostrictive effects is not fully understood, it is generally believed that the electrostrictive effect in these materials is due to the field-activated coalescence of micropolar regions to macrodomains of the parent ferroelectric.^{23,25} Consequently, the mechanism is essentially the same as the nonpolar, cubic prototype of the ferroelectric phase undergoing a momentary phase transformation to the ferroelectric phase while under the influence of an electric field. Furthermore, because a higher applied electric field leads to a larger magnitude of the induced ferroelectric polarization and strain, one is able to use this effect for achieving voltage-dependent dielectric, piezoelectric, pyroelectric, and electrooptic properties in ceramics. Longitudinal strains as high as 0.1% in PMN and 0.3% for PLZT (La/Zr/Ti = 9/65/35) have been reported for these electrostrictive materials.

Electrostriction-like effects are also evident in nonpolar, antiferroelectric (antipolar adjacent unit cells) materials that undergo a phase change from antiferroelectric (AFE) to ferroelectric when a sufficiently high electric field is applied. Although this effect is very abrupt (occurring suddenly at a specific voltage) in a material such as lead stannate zirconate titanate (PSZT), in another ceramic, such as PLZT, the change is “washed out” over a range of voltages; i.e., the former is more digital, and the latter is more analog. Longitudinal strains as high as 0.8% have been reported in these antiferroelectric materials.²⁶

(7) Electrooptic Effects

The electrooptic properties of PLZT materials are intimately related to their ferroelectric properties. Consequently, varying the ferroelectric polarization with an electric field, such as in a hysteresis loop, also produces a change in the optical properties of the ceramic. Moreover, the magnitude of the observed electrooptic effect is dependent on both the strength and direction of the electric field.

PLZT ceramics display optically uniaxial properties on a microscopic scale, and also on a macroscopic scale when polarized or activated with an electric field. There is one unique symmetry axis in uniaxial crystals, the optic axis (colinear with the ferroelectric polarization vector in ceramic PLZT), which possesses optical properties different from the other two orthogonal axes. That is, light traveling in a direction along the optical axis and vibrating in a direction perpendicular to it possesses an index of refraction (n_o) different from light traveling in a direction 90° to the optic axis and vibrating parallel to it (n_e). The absolute difference between the two indexes is defined as the birefringence; i.e., $n_e - n_o = \Delta n$. On a macroscopic scale, Δn is equal to zero before poling and has some finite value after poling, depending on the composition and the degree of poling. With relaxor materials, Δn is not permanent but exists only as long as the electric field is present.²⁷

A typical setup for determining the behavior of electrooptic ceramics is given in Fig. 4. Linearly polarized white light, on entering the electrically energized ceramic, is split in two orthogonally vibrating white light components (represented in Fig. 4 by red and green waves), whose vibration directions are defined by the crystallographic axes of the crystallites acting as one optical entity; in this case, the axes are defined by the direction of the electric field. Because of the different refractive indices, n_e and n_o , the propagation velocity of the two components is different within the material and results in a phase shift known as optical retardation. The total retardation (Γ) is a function of both Δn and the optical path length (t), according to the relationship

$$\Gamma = \Delta n t \quad (10)$$

where t is the ceramic thickness along the optical path. In the case of white light (average wavelength of 0.55 μm), as shown in Fig. 4, when sufficient voltage is applied to the ceramic, a half-wave retardation is achieved for one component relative to the other. The net result is one of rotating the vibration direction of the polarized light by 90°, thus allowing it to be trans-

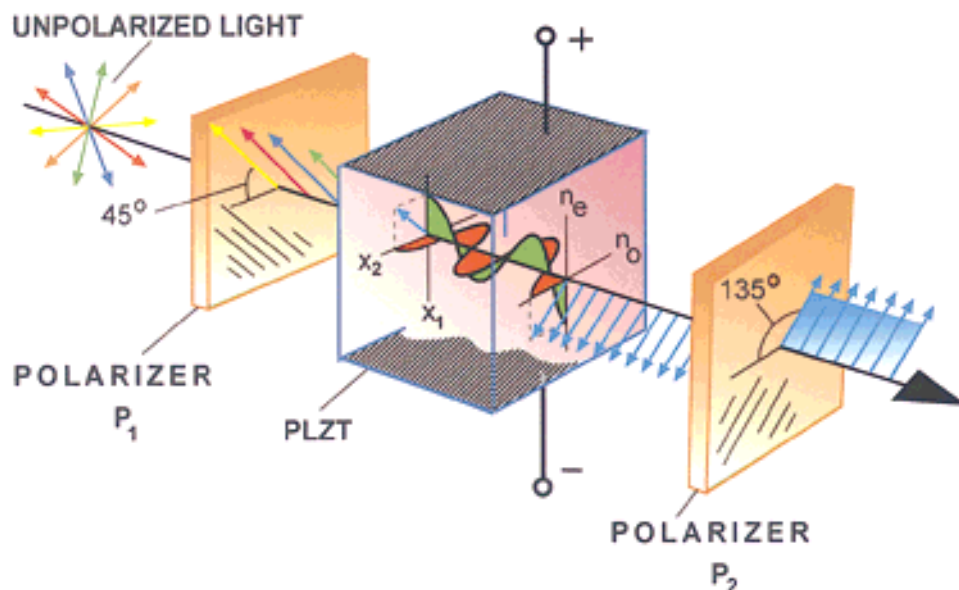


Fig. 4. Basic setup for evaluating electrooptic shutter/modulator characteristics (open condition shown).

mitted by the second (crossed) polarizer. Switching of the ceramic from a state of zero retardation (no voltage) to half-wave (full voltage) creates an ON/OFF light shutter, whereas selection of intermediate voltages create an analog modulator. Color generation (yellow, red, blue, and green) from the incoming white light can be achieved by increasing the voltage beyond half-wavelength; however, if monochromatic light is used, extending the voltage beyond half-wavelength results only in a progression of repeating light and dark bands, as in an interferometer.

There are two common types of electrooptic birefringent effects within the PLZT compositional phase diagram, i.e., (1) nonmemory quadratic (Kerr effect) and (2) memory linear (Pockel effect). The respective electrooptic coefficients for these effects are calculated from the following relationships:

$$R = -\frac{2\Gamma}{n^3 t E^2} \quad (11)$$

$$r_c = -\frac{2\Gamma}{n^3 t E} \quad (12)$$

where R is the quadratic coefficient, r_c the linear coefficient, and n the index of refraction ($n = 2.5$ for PLZT). If a polished, thin plate or a film-on-substrate is to be evaluated rather than a cube of bulk material, interdigital electrodes are often applied to the free surface of the material as opposed to the completely transverse electrodes shown in Fig. 4; in this case, the coefficients obtained are only a close approximation to the true coefficients, because the electric field lines are not truly transverse, but, rather, they are constrained to penetrate the material in a nonlinear manner.

II. Materials

(1) Barium Titanate Ceramics

BaTiO₃ is the first piezoelectric transducer ceramic ever developed; however, its use in recent years has shifted away from transducers to an almost exclusive use as high-dielectric-constant capacitors of the discrete and multilayer (MLC) types. The reasons for this are primarily twofold: (1) its relatively low T_C of 120°C, which limits its use as high-power transducers, and (2) its low electromechanical coupling factor in comparison to PZT (0.35 vs 0.65), which limits its operational output. Unlike PZT, which is a solid-solution composition containing a volatile component (PbO), BaTiO₃ is a definite chemical compound possessing relatively-high-stability components, making it easy to sinter while maintaining good chemical stoichiometry. Nevertheless, these materials are not actually used in their true chemical form, but, rather, are combined with special additives to modify and improve their basic properties. The additives for BaTiO₃ transducers usually are Sr²⁺ for varying the T_C downward from 120°C, Pb²⁺ for varying the T_C upward, Ca²⁺ for increasing the temperature range of stability of the tetragonal phase, and Co²⁺ for decreasing the high-electric-field losses without affecting the piezoelectric constants.

When BaTiO₃ is used in its primary application as a capacitor, a different group of additives is used, because the intent in this case is to suppress the ferroelectric and piezoelectric properties as much as possible while maintaining or increasing its dielectric constant. Two general types of modifiers are commonly used: T_C shifters and T_C depressors. The T_C shifters, such as SrTiO₃, CaZrO₃, PbTiO₃, and BaSnO₃, have the effect of shifting T_C to a higher or lower value, depending of the intended result. However, it is usually the case that a lower T_C is desired, such that the higher permittivity values associated with the T_C occur nearer room temperature or the temperature of operation. Depressors, such as Bi₂(SnO₂)₃, MgZrO₃, CaTiO₃, NiSnO₃, as well as the shifters, are added in small (1–8 wt%) quantities to the base BaTiO₃ composition to lower

or depress the sharpness of the dielectric constant peak at the T_C , thus giving a flatter dielectric constant–temperature profile. The net results of these efforts is to produce ceramic capacitors with dielectric constants up to 3000, loss tangents of ~1% or less, and temperature stabilities of ±15% for the X7R-type capacitors. Higher dielectric constants (to 12 000) can be achieved with a concurrent loss in temperature stability (+22%/–56%) for the Z5U-type capacitor, as designated by the Electronic Industries Association (EIA).²⁸

Dielectric constants in the range of 100 000 have been achieved with BaTiO₃-based compositions that also contain special additives to suppress the ferroelectric properties and facilitate the development of a chemically reduced material with semiconducting properties. These are the barrier-layer capacitors (BLCs).²⁹ These BLCs are produced by carefully reoxidizing a thin barrier layer in the boundary between each of the individual semiconducting grains of the ceramic, and it is these many insulating boundary layers that actually make up the capacitor. Because these barrier-layer thicknesses are measured in at ~1–2 μm, this type of capacitor is limited to <50 V.

Another type of material that was developed as early as 1955 from a BaTiO₃ base is the PTC ceramic possessing electrically conducting properties at room temperature and rather abruptly changing to a highly resistive material at some elevated temperature at $T_C \approx 120^\circ\text{C}$.^{30,31} Changing the T_C with appropriate additives, as mentioned previously for capacitors, changes the temperature at which this PTC resistivity anomaly occurs. This effect is exactly opposite to the more-common effect in the negative temperature coefficient (NTC) materials, which experience a reduction in resistance on increasing temperature. In the case of the PTCs, a small (0.2 mol%) addition of an off-valent additive, such as Y³⁺ or La³⁺, is used to produce an electrically semiconducting body without totally destroying the ferroelectric properties of the material, even though one is not able to ascertain ferroelectricity because of its conductivity. In fact, it is believed that the spontaneous polarization developed at the T_C nullifies or lowers the height of the barrier at the boundary of the grains, thereby allowing easy passage of current at temperatures below T_C . When the temperature is increased through the T_C , spontaneous polarization disappears, and the barrier height is again raised, leading to an increased resistance of ~6 or 7 orders of magnitude. The barriers on the surface of the grains (grain boundaries) are produced by sintering and cooling the material on a rigid schedule to produce a controlled oxidized layer. Applications include switches, sensors, motor starters, and controllers. Incidentally, the PTC effect is one of the few examples where a ceramic property in a material surpasses that of the corresponding single crystal, because the effect is absent in single crystals because there are no grain boundaries.

(2) PZT and PLZT Ceramics

Ferroelectric ceramics for piezoelectric applications historically have been formulated from a number of compositions and solid solutions including BaTiO₃, PZT, PLZT, PbN₂O₆, NaNbO₃, and PT. Foremost of these has been BaTiO₃, which dates from the early 1940s, but, in the past several decades, it largely has been supplanted by the PZTs and PLZTs for transducer applications.^{13,32,33} This is because PZT and PLZT compositions (1) possess higher electromechanical coupling coefficients than BaTiO₃, (2) have higher T_C values, which permit higher temperatures of operation or higher temperatures of processing during the fabrication of devices, (3) can be easily poled, (4) possess a wide range of dielectric constants, (5) are relatively easy to sinter at lower temperatures than BaTiO₃, and (6) form solid-solution compositions with many different constituents, thus allowing a wide range of achievable properties.

PZT ceramics are almost always used with a dopant, a modifier, or other chemical constituent or constituents to improve and optimize their basic properties for specific applications.^{13,19,34} Examples of these additives include off-valent donors, such as Nb⁵⁺ replacing Zr⁴⁺ or La³⁺ replacing Pb²⁺, to

counteract the natural *p*-type conductivity of the PZT and, thus, increase the electrical resistivity of the materials by at least 3 orders of magnitude. The donors are usually compensated by A-site vacancies. These additives (and vacancies) enhance domain reorientation; ceramics produced with these additives are characterized by square hysteresis loops, low coercive fields, high remanent polarization, high dielectric constants, maximum coupling factors, higher dielectric loss, high mechanical compliance, and reduced aging.

Off-valent *acceptors*, such as Fe^{3+} replacing Zr^{4+} or Ti^{4+} , are compensated by oxygen vacancies and usually have only limited solubility in the lattice. Domain reorientation is limited, and, hence, ceramics with acceptor additives are characterized by poorly developed hysteresis loops, lower dielectric constants, low dielectric losses, low compliances, and higher aging rates.

Isovalent additives, such as Ba^{2+} or Sr^{2+} replacing Pb^{2+} or Sn^{4+} replacing Zr^{4+} or Ti^{4+} , in which the substituting ion is of the same valency and approximately the same size as the replaced ion, usually produce inhibited domain reorientation and poorly developed hysteresis loops. Other properties include lower dielectric loss, low compliance, and higher aging rates.

Dopants are usually added in concentrations of ≤ 3 at.%. *Modifiers* are substituted into the original PZT composition as solid-solution constituents in concentrations of ≥ 5 at.%. The most common examples of modifier systems are (Pb,La) , $(\text{Zr},\text{Ti})\text{O}_3$, $(\text{Pb},\text{Sr})(\text{Zr},\text{Ti})\text{O}_3$, $(\text{Pb},\text{Ba})(\text{Zr},\text{Ti})\text{O}_3$, $\text{Pb}(\text{Zr},\text{Ti},\text{Sn})\text{O}_3$, $(\text{Pb},\text{La})\text{TiO}_3$, and $\text{Pb}(\text{Mg},\text{Nb})\text{O}_3\text{--PbZrO}_3\text{--PbTiO}_3$, although, in actuality, there are many of these lead-containing, solid-solution systems.¹³ One system that embraces

all compositional aspects of the dielectric, piezoelectric, pyroelectric, ferroelectric, and electrooptic ceramics is the PLZT system.³⁵ Figure 5 shows the PLZT system with the parent PZT phase diagram. Several areas on the diagram are color coded for easy identification: (1) the ferroelectric tetragonal and rhombohedral phases are shown in orange, (2) the orthorhombic antiferroelectric phase in purple, (3) the cubic paraelectric (PE; nonferroelectric) phases in white, (4) the morphotropic phase boundary (MPB) in magenta, (5) the pyroelectric application areas near PbTiO_3 in blue, (6) the economically important MPB compositions that embrace almost all of the transducer applications in green, (7) the compositional area for AFE-to-FE, enforced-phase devices in gray, and (8) specific compositions in these regions in yellow.

Figure 5 shows that the effect of adding lanthanum to the PZT system is (1) one of maintaining extensive solid solution throughout the system and (2) one of decreasing the stability of the ferroelectric phases in favor of the paraelectric and antiferroelectric phases, as indicated by the red line, which shows the reduction of the T_C with increasing lanthanum. At a 65/35 ratio of PZ/PT (where PZ is lead zirconate, PbZrO_3), a concentration of 9.0% lanthanum (designated as 9/65/35) is sufficient to reduce the temperature of the stable ferroelectric polarization to slightly below room temperature, resulting in a material that is nonferroelectric and cubic in its virgin state. The cross-hatched area existing along the FE-PE phase boundary denotes a region of diffuse, metastable relaxor phases that can be electrically induced to a ferroelectric phase. Materials within this region exhibit a quadratic strain and electrooptic behavior.

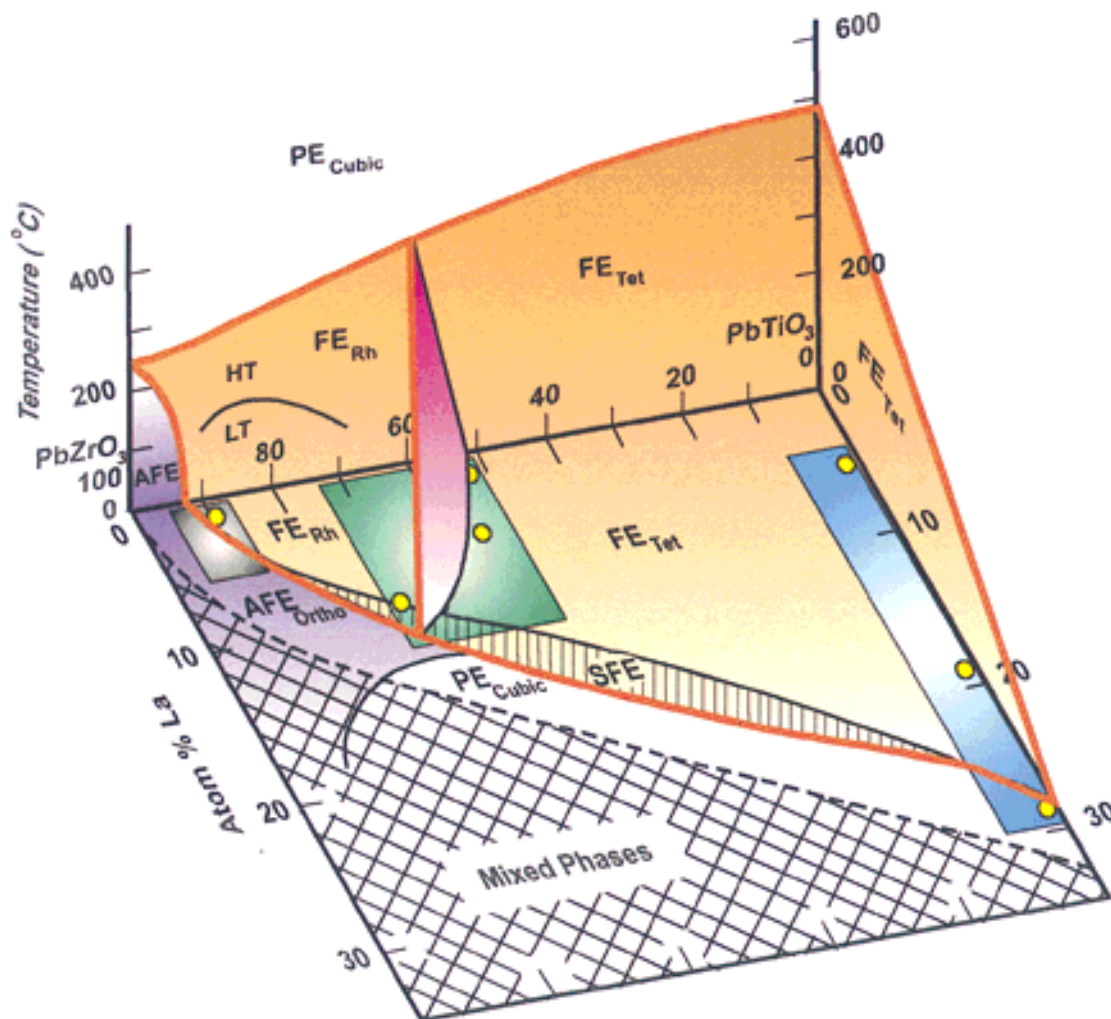


Fig. 5. Phase diagram of the PZT and PLZT solid-solution systems.

The solubility of lanthanum in the PZT lattice is a function of composition and is related directly to the amount of PT present. The compositional dependence of the solubility limit is indicated by the dashed line adjacent to the mixed-phase region (double cross-hatched area) in Fig. 5. For the two end-member compositions, PZ and PT, these limits are 4 and 32 at.%, respectively. The solubility limits for intermediate compositions are proportional to their Zr/Ti ratios.

Modification of the PZT system by the addition of lanthanum sesquioxide has a marked beneficial effect on several of the basic properties of the material, such as increased squareness of the hysteresis loop, decreased coercive field, increased dielectric constant, maximum coupling coefficients, increased mechanical compliance, and enhanced optical transparency. The optical transparency was discovered in the late 1960s as a result of an in-depth study of various additives to the PZT system.³⁵ Results from this work indicate that La^{3+} , as a chemical modifier, is unique among the off-valent additives in producing transparency. The reason for this behavior is not fully understood; however, it is known that lanthanum is, to a large extent, effective because of its high solubility in the oxygen octahedral structure, thus producing an extensive series of single-phase, solid-solution compositions. The mechanism is believed to be one of lowering the distortion of the unit cell, thereby reducing the optical anisotropy of the unit cell and, at the same time, promoting uniform grain growth and densification of a single-phase, pore-free microstructure.

Electrooptic compositions in the PLZT phase diagram are generally divided into three application areas: (1) nonmemory quadratic, (2) memory, and (3) linear. As mentioned previously, the quadratic materials are located along the FE-PE phase boundary, principally in the cross-hatched area. Memory compositions having stable, electrically switchable polarization and optical states are largely located in the ferroelectric rhombohedral phase region, and the linear materials possessing non-switching, linear strain, and electrooptic effects are confined to the area encompassing the tetragonal phase.

(3) PMN Ceramics

Although the study of relaxor materials began in the early 1960s with work on single-crystal $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) materials³⁶ and continued in the mid-1960s with PMN as one of the triaxial components in the PZ-PT-PMN solid-solution system,³⁷ more-recent work in the early 1980s with PMN-based relaxor ceramics has led to their successful application as high-strain (0.1%) electrostrictive actuators^{38,39} and high-dielectric-constant ($>25\,000$) capacitors.⁴⁰ The phase diagram for this system is given in Fig. 6. The most popular specific composition in this system is $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.1\text{PbTiO}_3$, which is PMN containing 10% PT, thus increasing the T_m (the temperature of maximum dielectric constant for relaxors,

equivalent to T_C for normal ferroelectrics) of PMN to $\sim 40^\circ\text{C}$. For this composition, the temperature of polarization loss (T_d) is $\sim 10^\circ\text{C}$; hence, the material is a relaxor at room temperature (25°C). An addition of $\sim 28\%$ PT causes the material to revert to a normal ferroelectric tetragonal phase with $T_C \approx 130^\circ\text{C}$.

Unlike PZT and PLZT, PMN ceramics are somewhat difficult to prepare in a phase-pure condition. Several methods of powder preparation have been developed over the years to reduce the undesirable pyrochlore phase to a bare minimum,⁴¹ but the process that has met with consistent success is the so-called columbite precursor method.⁴² In this technique, MgO and Nb_2O_5 are first reacted to form the columbite structure, MgNb_2O_6 , which is then reacted with PbO and TiO_2 to form the PMN-PT compositions.

(4) Ferroelectric Films

The 1970s and 1980s witnessed the emergence of thin and thick films (both ferroelectric and nonferroelectric) as an important category of materials that was brought about by the maturing of laser and transistor technologies (e.g., optical fibers, integrated optics, microelectromechanical systems, microprocessors, and computers) and promises to be the springboard for the age of integration beyond the 1990s into the next century.^{43,44} New materials development during this time period was one of form (i.e., from bulk to films) rather than composition. Almost all of the current compositions that are used in the fabrication of films had their beginnings in the bulk materials. Examples of these include BaTiO_3 , barium strontium titanate, PZT, PLZT, PNZT(Nb), PSZT(Sn), PBZT(Ba), PT, bismuth titanate, lithium niobate, barium strontium niobate, strontium barium tantalate, and potassium niobate. Thus, one can say (at least for the present time) that an adequate number of ferroelectric compositions now exist and are being produced as good-quality, polycrystalline thin and thick films by a variety of forming methods. These films will form the basis for the development of new structures and devices well beyond the turn of the century.

III. Processing

(1) Powder Preparation

Ferroelectric ceramics are traditionally made from powders formulated from individual oxides; however, the newer electrooptic materials and some of the PTC ceramics utilize chemical coprecipitation⁴⁵⁻⁴⁷ or hydrothermal⁴⁸ techniques. The processing method that one selects to prepare the powders depends, to a large extent, on cost, but even more important is the end application. Understandably, electrooptic ceramics require higher-purity, more-homogeneous, and higher-reactivity powders than do the piezoelectric ceramics, because inhomogeneities can be detected optically much more easily than electrically. As a result, different powder process techniques have evolved in the two cases. Piezoelectric ceramics continue to be prepared from the most economical, mixed-oxide (MO) process,³⁴ whereas the optical ceramics utilize specially developed chemical coprecipitation (CP) processes²⁷ involving liquid inorganic or organometallic precursors. Although not yet fully achieved, the trends in this area are toward the development of one unified process that meets the objectives of both types of materials. There is a commonality in these objectives, because the more recent piezoelectric devices demand higher-quality material (essentially zero porosity), and the electrooptics require a more economical process.

A flowsheet describing the essential steps for both the MO and CP processes is given in Fig. 7. There are many steps that are common to both methods. The essential differences between the two methods occur in the powder forming and densification stages. In the MO methods, this very simply consists of wet milling (slurry form) the individual oxides or other compounds, such as the carbonates or nitrates that decompose to the oxides during calcining (a high-temperature solid-state

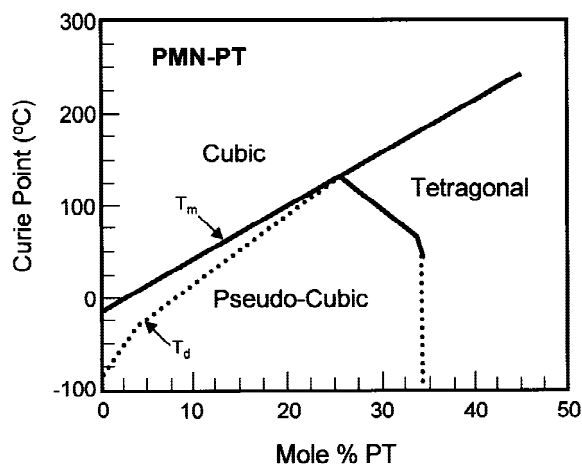


Fig. 6. Phase diagram of the PMN-PT solid-solution system.²⁴

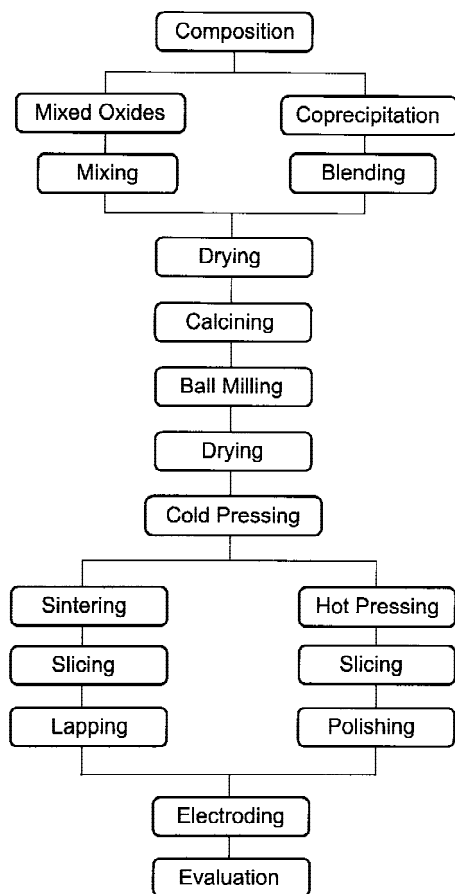


Fig. 7. Flow sheet for processing of piezoelectric and electrooptic ceramics.

chemical reaction) at 800°–900°C. In the CP method, the starting materials are usually solutions that are mutually soluble in each other, thus producing an atomically homogeneous precursor solution that is precipitated while blending. Because the particle sizes of the CP powders are usually much finer than the MO powders, (0.03–0.1 μm vs 1 μm), the CP powders are more reactive and are calcined at a lower temperature, ~500°C for 1 h.

Ball milling of the calcined material is necessary for both types of powders to produce the required chemical and optical homogeneity. This is a very critical step in the process, because too little milling does not produce the necessary homogeneity, and over milling increases the likelihood of contamination leading to optical scattering. A common practice is to use a plastic-lined mill with high-density media (alumina or zirconia balls) and a nonpolar, nonflammable milling liquid, such as trichloroethylene or freon TF, for the electrooptic materials; however, distilled water is a better liquid for piezoelectrics from a cost and environmentally preferred standpoint. Depending on the particular powder characteristics, milling times may vary from 2 to 16 h. The milled powders are then thoroughly dried, mechanically broken up, homogenized in a V-blender, and stored for further processing.

(2) Forming and Firing (Densification)

There are a variety of forming methods that have been developed over the years that have been successfully used in compacting the powders to a specific form or shape prior to densification. Cold pressing in a steel mold is, perhaps, the oldest and most economical of these methods and, thus, is given in Fig. 7; there are, however, several more methods, including extrusion, slip casting, tape casting, roll compaction, screen printing, and injection molding. All of these techniques

are currently used with excellent success, and the choice of one over the other is usually made on the basis of cost and convenience for the end application. For details on these techniques, it is suggested that the reader consult various excellent texts on the subject.^{40,49,50}

In addition to composition and powder preparation, densification of the powder into a pore-free, fully dense ceramic element is the third area of processing that is extremely critical to achieving a high-quality product. The flowsheet in Fig. 7 shows two methods, i.e., conventional sintering and hot pressing. Of these two, sintering is, by far, the oldest and most economical method of consolidation, but it has its limitations when it comes to achieving full density. Full density is rarely achieved with conventional sintering of ferroelectric ceramics unless special techniques are used to assist the sintering process during firing. An example of this is the use of an oxygen atmosphere for sintering lead-containing ceramics, such as PZT and PLZT.⁵¹ With air atmosphere only, densities of ~96% of theoretical can be achieved, but with an oxygen atmosphere, this value can approach 99%. Another example is the use of excess PbO during sintering to compensate for PbO loss (volatilization) as well as providing for higher densification rates via liquid-phase sintering. When both of these techniques are used, bulk densities approaching 100% can be achieved, as evidenced by the high optical transparency obtained in PLZT 9/65/35 sintered ceramics.⁵² Typical sintering conditions for conventional PZT are 1250°C for 5 h with flowing oxygen and 60 h for transparent PLZT.

Although oxygen-atmosphere sintering can and does produce fully dense and transparent ceramics when the proper procedures are used, there continues to exist a problem with this process in consistently achieving high optical transparency. On the other hand, hot pressing is a viable method of producing fully dense ceramics, and its worth has been proved over several decades of experience. Slugs of PLZT as large as 150 mm (6 in.) in diameter and 25 mm (1 in.) in thickness are regularly hot-pressed to full density and high transparency. Typical hot-pressing conditions are 1250°C for 16 h at 14 MPa (2000 psi).

Other densification methods that have proved to be successful for ferroelectric ceramics in more recent years are (1) hot isostatic pressing, (2) vacuum sintering, and (3) a two-step process of sintering and then hot isostatic pressing. The two-step technique involving presintering was developed to eliminate the need for a cladding enclosure in the final gas isostatic hot pressing step.

After densification, the final steps involved in the processing of ferroelectric ceramics (Fig. 7) are (1) slicing of the slug, (2) lapping of the slices, (3) polishing of the plates for electrooptic elements, (4) electroding, and (5) evaluation of the parts for further assembly to components.

Some typical samples of hot-pressed and sintered PLZT and PZT ceramics are shown in Fig. 8 with thick (12 μm) films on sapphire (round substrate) and glass (rectangular substrate). The transparent part on the "sintered ceramic" label is a fully dense, oxygen-sintered, PLZT 9/65/35 ceramic.

(3) RAINBOW Processing

The latest development in the processing of bulk materials consists of the high-temperature chemical reduction of high lead-containing ferroelectric wafers to produce strain-amplified wafer actuators called RAINBOWS, an acronym for reduced and internally biased oxide wafer.⁵³ More specifically, this technology involves the local reduction of one surface of a ceramic wafer, thereby achieving an anisotropic, stress-biased, dome or saddle-shaped configuration with significant internal tensile and compressive stresses that act to amplify the axial motion of the wafer and also increase the overall strength of the material. After reduction, the flat wafer changes its shape to one that resembles a contact lens. This is believed to be due to (1) the reduction in the volume of the reduced layer (largely metallic lead) compared to the unreduced material, (2) the dif-



Fig. 8. Typical examples of PLZT and PZT ceramics and films.

ferential thermal contraction between the reduced and unreduced layers on cooling to room temperature, and (3) the volume change in going from the paraelectric to ferroelectric state at its T_C .

Typical steps for the RAINBOW process involve placing a flat wafer on a graphite block, inserting the block and wafer into a furnace preheated to 975°C, leaving it there for 1 h and then removing it for cooling to room temperature in ~45 min. The net result is a monolithic (monomorph) structure consisting of an unreduced piezoelectric (ferroelectric) layer that is highly stressed, primarily in compression, and an electrically conducting reduced layer that produces the stress. These internal stresses have been shown to be instrumental in achieving unusually high axial bending displacement as well as enhanced load-bearing capability.^{54,55}

(4) Thin- and Thick-Film Processing

The various techniques that are currently available for the fabrication of thin films are noticeably more varied in type and in sophistication than a couple of decades ago. Better equipment and more advanced techniques have, undoubtedly, led to higher-quality films and may be a primary factor in the now routine achievement of ferroelectricity in films as thin as 0.1 μm and as thick as 22 μm prepared by a selection of different methods. Table II lists the major methods presently used to produce ferroelectric films. Reviews of the details concerning most of these techniques are given in previous publications.^{44,56-61}

In general, there are two major categories of deposition techniques for films: (1) physical vapor deposition and (2) chemical processes involving chemical vapor deposition (CVD) and chemical solution deposition. The first of these requires a vacuum to obtain a sufficient flux of atoms or ions capable of depositing onto a substrate, whereas the second usually does

not; thus, one can roughly identify these two categories as vacuum and nonvacuum techniques, respectively. The advantages of the vacuum methods are (1) dry processing, (2) high purity and cleanliness, (3) compatibility with semiconductor integrated-circuit (IC) processing, and (4) possible epitaxial film growth; however, these are offset by disadvantages, such as (1) slow deposition rates, (2) difficult stoichiometry control in ferroelectric multicomponent systems, where evaporation or sputtering rates differ considerably, (3) high-temperature post-deposition anneal, often required for crystallization, and (4) high-capital equipment acquisition and maintenance costs.

The chemical techniques are usually characterized by (1) higher deposition rates, (2) good stoichiometry control, (3) large area, pinhole-free films, and (4) lower initial equipment costs. These advantages, especially in the case of CVD and its many variations, would seem to preclude the use of vacuum methods; however, the limited availability and toxicity of some of the ferroelectric precursors have posed some problems for this method. Combining the advantages of excellent compositional control, spin-on/spray-on/dip-coating capability, and very low equipment costs, the wet chemical solution deposition techniques (sol-gel and MOD) already have been quite successful and extensively used in producing thin and thick films of PZT, PLZT, and many other materials. The ready availability, low cost, and water solubility of many of the precursors for the wet chemical methods have also significantly contributed to their popularity. Examples of some MOD acetate precursor solutions in the PZT system are shown in Fig. 9.

Some of the substrates that have been successfully used for the deposition of films include silicon, platinized silicon, sapphire, magnesia, strontium titanate, silver foil, lithium niobate, gallium arsenide, fused silica, zirconia, and glass.

IV. Properties

(1) Microstructure

Compositions in the PLZT system and to some degree in the PZT system, whether piezoelectric or electrooptic, are characterized by a highly uniform microstructure consisting of randomly oriented grains (crystallites) tightly bonded together. An example of such a microstructure is given in Figs. 10(A) and (B) for PLZT 9/65/35. The sample was polished and thermally etched at 1150°C for 1 h. As is typical for most PLZT hot-pressed microstructures, little or no entrapped porosity is evident. This is due to the influence of the external pressure during hot pressing, which aids in pore removal while the material is in a thermochemically active state at elevated temperatures. In actuality, some small amount of porosity exists in all the materials whether hot-pressed or atmosphere sintered; however, it is more important in the electrooptic than in the piezoelectric materials, because porosity in the 0.5–5 μm diameter range is quite effective in scattering light. Figure 10 also shows that the microstructure is very uniform, with an average grain size for this sample of ~8 μm . Piezoelectric ceramics usually possess grain sizes in the range of 2–6 μm , whereas the electrooptics cover a wider range from 2 to 10 μm , depending on their intended application. A uniform grain size is a highly desirable feature from the standpoint of performance.

Table II. Thin- and Thick-Film Deposition Techniques

Physical vapor deposition
Sputtering (rf magnetron, dc, ion beam)
Evaporation (e-beam, resistance, molecular beam epitaxy)
Laser ablation
Chemical vapor deposition (CVD)
MOCVD (metal-organic CVD)
PECVD (plasma-enhanced CVD)
LPCVD (low-pressure CVD)
Chemical solution deposition
Sol-gel (solution-gelation)
MOD (metalloorganic decomposition)
Melt solution deposition
LPE (liquid-phase epitaxy)

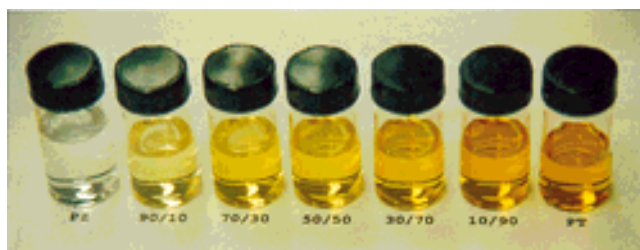


Fig. 9. Acetate precursor solutions in the PZT compositional system.

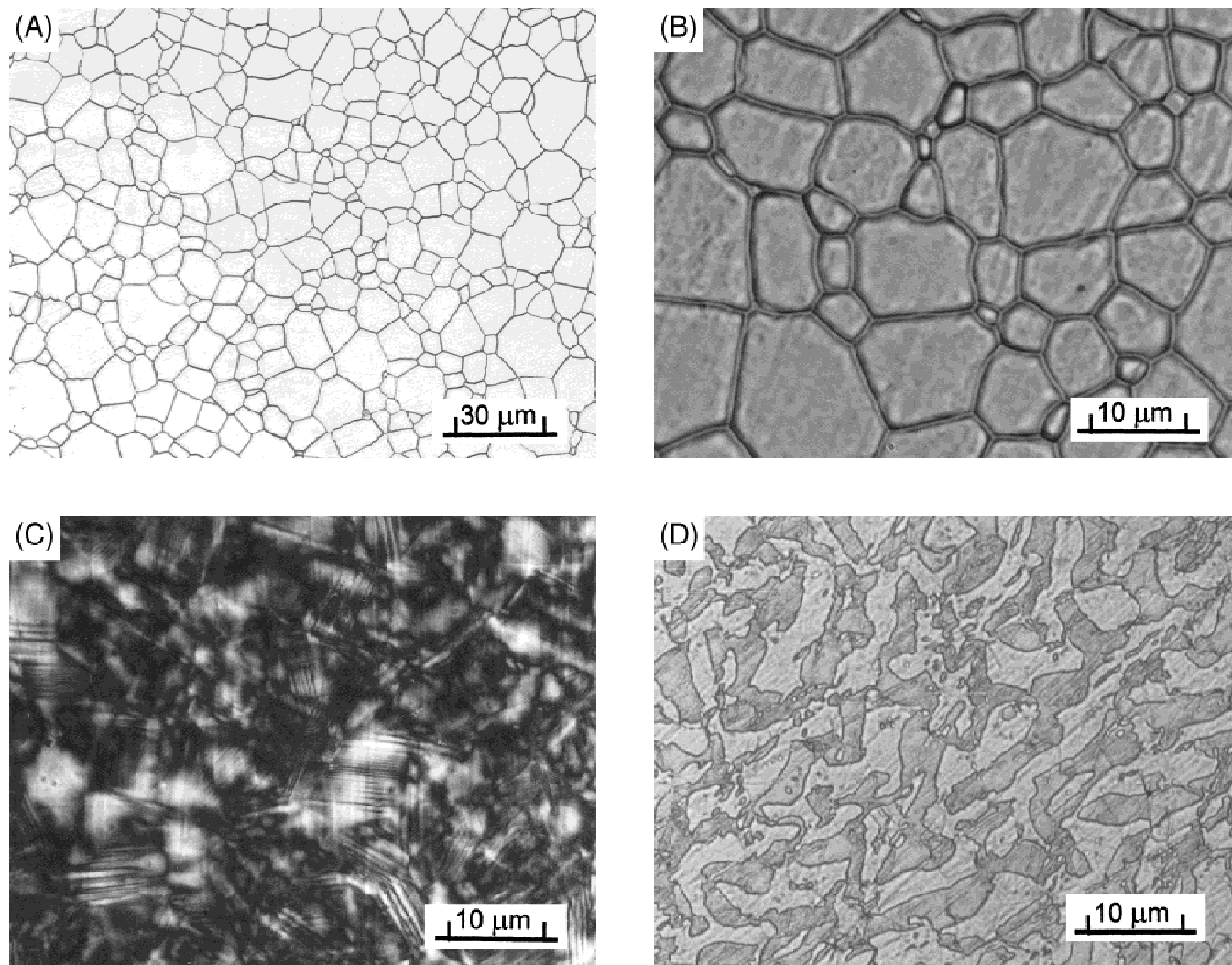


Fig. 10. Typical microstructures of (A) hot-pressed electrooptic PLZT 9/65/35, (B) hot-pressed electrooptic PLZT 9/65/35 at higher magnification, (C) hot-pressed PLZT 12/40/60 in transmitted light, and (D) chemically etched PLZT 7/65/35 in reflected light.

Domain patterns, i.e., regions of uniform and homogeneous spontaneous polarization within a grain or between several grains, also can be revealed in the microstructure of a ferroelectric memory ceramic when transmitted light or reflective light and chemical etching techniques are used. Examples of these domain patterns are shown in Figs. 10(C) and (D), respectively, for materials with an average grain size of 8 μm. Figure 10(C) shows that a predominance of 90° domains is evident in the tetragonal PLZT 12/40/60 ceramic, whereas the domains of rhombohedral PLZT 7/65/35 in Fig. 10(D) are mostly 180°. The domains in 7/65/35 show up as a bilevel structure, because one end of the electric dipole chemically etches faster than the opposite end. Distinctive features here are (1) absence of etched grain boundaries because of the fully dense structure and (2) bridging of grain boundaries by domains, indicating little disorder at the boundaries, (these predominantly 180° domains are ~3 μm × 15 μm in size). No domains are observed in the microstructure of the 9/65/35 material in Fig. 10(A), because this polished section was thermally etched and not chemically etched; i.e., it was etched at 1150°C, where domains do not exist.

(2) Electrical Properties

(A) *Dielectric Properties:* Because almost all of the useful properties of ferroelectric ceramics are related in some manner to their response with an electric field, the electrical behavior of these materials is important to their successful

application in dielectric, piezoelectric, pyroelectric, or electrooptic devices. Ferroelectrics are, in general, characterized by (1) higher dielectric constants (200–10 000) than ordinary insulating substances (5–100), making them useful as capacitor and energy-storage materials, (2) relatively low dielectric loss (0.1%–7%), (3) high specific electrical resistivity ($>10^{13} \Omega \cdot \text{cm}$), (4) moderate dielectric breakdown (100–120 kV/cm for bulk and 500–800 kV/cm for thin films), and (5) nonlinear electrical, electromechanical, and electrooptic behavior. Not all of these properties are optimized and realized in a given material of chemical composition, and, hence, a variety of ceramic materials are manufactured and are available from several different companies throughout the world. A summary of typical properties for selected compositions is given in Table III.

Small-signal (1 kHz) relative dielectric constant values for several selected compositions are given in Table III. They range from a low of 225 for lead niobate to a high of 24 000 for PMN–PT (90/10). Values for the PZT and PLZT compositions are intermediate, ranging from 1300 for PZT-4 (a hard, A-site-substituted piezo material) to 5700 for a phase-boundary, relaxor PLZT material. The loss tangents ($\tan \delta$) vary in value from 0.4% to 6% for the various ceramics, and, in general, the lower loss factors are associated with the lower dielectric constants.

(B) *Hysteresis Loops:* The hysteresis loop (polarization versus electric field) is the single most important measurement that can be made on a ferroelectric ceramic when characteriz-

Table III. Compositions and Properties of Typical Ferroelectric Ceramics[†]

Composition	Density (g/cm ³)	T _C (°C)	K	tan δ (%)	k _p	k ₃₃	d ₃₃ (×10 ⁻¹² C/N)	d ₃₁ (×10 ⁻¹² C/N)	g ₃₃ (×10 ⁻³ V·m/N)	s ₁₁ ^E (×10 ⁻¹² m ² /N)	Q ₁₁ (m ² /C ²)	Q ₁₂ (m ² /C ²)	m ₁₁ (×10 ⁻¹⁶ m ² /V ²)	m ₁₂ (×10 ⁻¹⁶ m ² /V ²)	R (×10 ⁻¹⁶ m ² /V ²)	r _C (×10 ⁻¹⁰ m/V)
BaTiO ₃	5.7	115	1700	0.5	0.36	0.5	190	-78	11.4	9.1						0.28
PZT-4	7.5	328	1300	0.4	0.58	0.7	289	-123	26.1	12.3						
PZT-5A	7.8	365	1700	2.0	0.6	0.71	374	-171	24.8	16.4						
PZT-5H	7.5	193	3400	4.0	0.65	0.75	593	-274	23.1	16.5						
PMN-PT (65/35)	7.6	185	3640	0.58	0.58	0.70	563	-241		15.2						
PMN-PT (90/10)	7.6	40	24000	5.5	0	0	0	0	0		0.016	-0.008	3.6	1.7		
PbNb ₂ O ₆	6.0	570	225	1.0	0.07	0.38	85	-9	43.1	25.4						
(Na _{0.5} K _{0.5})NbO ₃	4.5	420	496	1.4	0.46	0.61	127	-51	29.5	8.2						1.0
PLZT 7/60/40	7.8	160	2590	1.9	0.72		710	-262	22.2	16.8						1.2
PLZT 8/40/60	7.8	245	980	1.2	0.34											
PLZT 12/40/60	7.7	145	1300	1.3	0.47		235		12	7.5						
PLZT 7/65/35	7.8	150	1850	1.8	0.62		400		22	13.5	0.022	-0.012				
PLZT 8/65/35	7.8	110	3400	3.0	0.65		682		20	12.4	0.018	-0.008				
PLZT 9/65/35	7.8	80	5700	6.0	0	0	0	0	0		0.020	-0.010	5.8	3.6	3.8	0
PLZT 9.5/65/35	7.8	75	5500	5.5	0	0	0	0	0		0.021	-0.009			1.5	0
PLZT 7.6/70/30	7.8	100	4940	5.4	0.65								11.7			
PLZT 8/70/30	7.8	85	5100	4.7	0	0	0	0	0		0.010	-0.008				

[†]Data compiled from Refs. 19, 22, 24, 27, 34, 35, 62, and 63.

ing its electrical behavior. This loop is very similar to the magnetic loop (magnetization versus magnetic field) one obtains from a ferromagnetic material; the very name "ferroelectric" has been appropriated from this similarity, even though there is no ferro, i.e., iron constituent, in ferroelectrics as a major component.

Hysteresis loops come in all sizes and shapes, and, similar to a fingerprint, identify the material in a very special way. Therefore, one should become familiar with such a measurement. Although early workers in the field of ferroelectrics utilized a dynamic (60 Hz) measurement with a Sawyer-Tower circuit and an oscilloscope readout, more-recent work usually has been done with a single-pulse or dc (~0.1 Hz) Sawyer-Tower measurement using an X-Y plotter or computer readout.²⁷ Typical hysteresis loops obtained from various ferroelectric ceramic materials are illustrated in Fig. 11: (A) a linear tracing from a BaTiO₃ capacitor, (B) a highly nonlinear loop from a low-coercive-field (soft) memory ferroelectric such as is found in the rhombohedral region of the PZT phase diagram, (C) a narrow, nonlinear loop obtained from a slim-loop ferroelectric (SFE) quadratic relaxor that is located in the FE-PE boundary region of the PLZT system, and (D) a double loop that typically is obtained from a nonmemory antiferroelectric material in the PSZT system.

The antiferroelectric materials are essentially nonpolar, non-ferroelectric ceramics that revert to a ferroelectric state when subjected to a sufficiently high electric field. Outwardly, they differ from the SFE relaxor materials in that (1) the dielectric constants usually are lower, (2) higher electric fields are usually required to induce the ferroelectric state, and (3) the onset of the ferroelectric state and the return of the antiferroelectric state are usually fairly abrupt, thus giving the loop an appearance of two subloops that are positively and negatively biased. These characteristics are shown in loop (D) in Fig. 11.

A considerable amount of information can be obtained from a hysteresis loop. Figure 11 also shows that (1) the loop in (B) reveals that the material has memory, whereas the loop in (C) indicates no memory, (2) high remanent polarization (P_R) relates to high internal polarizability, strain, electromechanical coupling, and electrooptic activity, (3) for a given material, the switching field (E_c) is an indication of the grain size for a given material (i.e., lower E_c means larger grain size and higher E_c means smaller grain size), (4) a high degree of loop squareness usually indicates better homogeneity and uniformity of grain size, (5) an off-centered loop from the zero voltage point (the loop is usually centered symmetrically around zero voltage) indicates some degree of internal electrical bias that may be caused by internal space charge and/or aging, (6) the sharpness

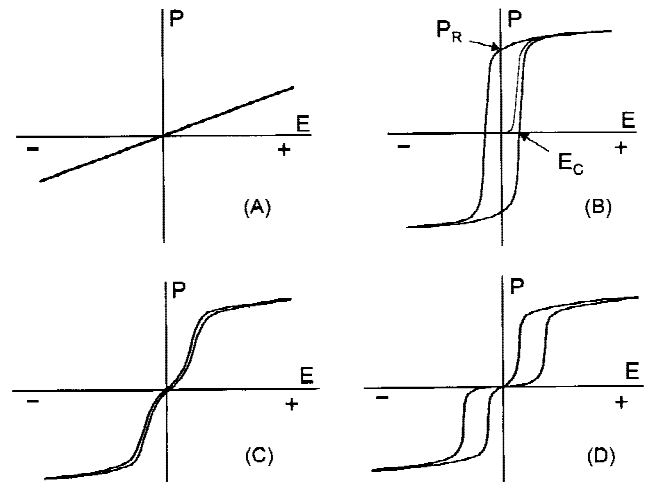


Fig. 11. Typical hysteresis loops from various ferroelectric ceramics: (A) BaTiO₃ capacitor, (B) soft (easily switchable) PZT, (C) PLZT 8.6/65/35 relaxor, and (D) PSZT antiferroelectric material.

of the loop tips indicates a high electrical resistivity ($>10^9 \Omega \cdot \text{cm}$), (7) high induced polarization in relaxor materials indicates high electrostriction strain and high electrooptic coefficients, (8) the slope of the P - E loop at any point along the loop is equal to the large-signal dielectric constant, (9) the opening up of the loop of a SFE relaxor material can indicate nonohmic contact between the electrodes and the ceramic, and (10) a sudden large change in "apparent" polarization is usually a result of incipient dielectric breakdown. Remanent polarizations for most of the lead-containing ferroelectrics typically vary from 30 to 40 $\mu\text{C}/\text{cm}^2$, whereas the coercive fields vary over quite a wide range, from $\sim 2 \text{ kV}/\text{cm}$ to near electrical breakdown ($\sim 125 \text{ kV}/\text{cm}$), depending on the type of dopants and modifiers added.

The strains associated with two of these materials (i.e., ferroelectric and SFE) on traversing their hysteresis loops are given in Fig. 12. In the ferroelectric case, the switching strain accompanying the polarization reversal process results in the familiar "butterfly" loop, with the remanent strain state in the center of the loop (point O). Positive voltage then results in a longitudinal expansion of the ceramic, whereas a negative voltage (less than the coercive field) results in a longitudinal contraction. This is known as the linear strain effect in piezoelectric materials and does not involve domain switching. For the SFE relaxor case, there is no remanent strain when the electric field is not applied, because, in this case, the rest position of the ion is in the center of the unit cell. However, when the field is applied, ionic movement (polarization) and strain occur simultaneously, both being dependent upon the strength of the field. Because the sign of the strain produced (positive for elongation) is the same regardless of the polarity of the field, this is the electrostrictive effect mentioned previously.

(C) *Piezoelectric and Electrostrictive Properties:* Compositions within the PZT and PLZT systems possess some of the highest electromechanical coupling coefficients attainable in ceramic materials. Some typical values of k_p , k_{33} , d_{33} , d_{31} , and g_{33} for these materials are given in Table III with BaTiO_3 and the niobates. Maximum values of k_p (0.72) and d_{33} ($710 \times 10^{-12} \text{ C}/\text{N}$) are found in the soft (easily switchable) PLZT composition 7/60/40. This composition is located within the morphotropic phase-boundary region separating the ferroelectric rhombohedral and tetragonal phases. Over the years, there has been considerable speculation concerning the reasons for this maximum in coupling at the MPB.^{64,65} These may be summarized as being due to (1) the existence of a mixture of phases at the boundary, (2) a concurrent maximum in dielectric

constant at the MPB, (3) a larger number of reorientable polarization directions existing in the MPB mixed-phase region, and (4) a maximum in mechanical compliance in the boundary region, permitting maximum domain reorientation without physically cracking.

Also included in Table III are some typical electrostrictive Q and m values for representative compositions. Table III shows that most Q_{11} coefficients are in a rather narrow range of 0.010 – $0.022 \text{ m}^4/\text{C}^2$, as are the Q_{12} coefficients in a range of 0.008 – $0.012 \text{ m}^4/\text{C}^2$. Also given are the Q values of two PLZT ferroelectric compositions (7/65/35 and 8/65/35) for comparison, pointing out the observation that the Q coefficients are similar in magnitude regardless of the ferroelectric or nonferroelectric nature of the material. This is because the Q coefficient relates the resulting strain to the electrically induced polarization, regardless of whether the material has permanent polarization.

The m coefficients, on the other hand, relate the strain to the electric field; hence, their values vary more widely, ranging from 1.7×10^{-16} to $11.7 \times 10^{-16} \text{ m}^2/\text{V}^2$.

(D) *Pyroelectric Properties:* Although the pyroelectric effect in crystalline materials has been known for many centuries, it has been within only the last four decades that this effect has been studied in ferroelectric ceramics.^{66–69} As mentioned previously, this effect occurs in polar materials and is manifested in a change in polarization as a function of temperature. This results in a reduction of the bound charge required for compensation of the reduced dipole moment on increasing temperature and vice versa on decreasing temperature; thus, the change in voltage on the material's electrodes is a measure of the change in the material's polarization due to absorbed thermal energy. A common figure-of-merit for pyroelectrics is

$$\text{FOM} = \frac{p}{c(K \tan \delta)^{1/2}} \quad (13)$$

where p is the pyroelectric charge coefficient, c the specific heat, and $\tan \delta$ the dielectric loss tangent. Maximizing the performance of a material then involves selecting a ceramic with a high pyroelectric coefficient and low specific heat, dielectric constant, and dielectric loss factor. This is difficult to achieve in a given material, and, most often, its performance is limited by the dielectric loss, which is reflected in a poor signal-to-noise ratio.

Two families of ceramics have dominated this area of endeavor: PZT and BST (barium strontium titanate) materials. However PLZT and PMN are also considered viable candidates. The former two materials are considered ferroelectric thermal detectors (absorbed energy generating the temperature-dependent change in polarization), whereas the latter two, as well as BST, can be considered dielectric bolometers (electrically induced, temperature-dependent change in dielectric constant materials).⁶⁸ Ceramics, in many cases, are considered better choices for thermal imaging applications than crystalline materials with higher pyroelectric coefficients because of their lower cost, availability, ease of processing, and good stability. These materials in bulk and thin-film forms are used in commercial products for law-enforcement, night surveillance, and security applications.

(E) *Optical and Electrooptic Properties:* Unlike the PZT ceramics and other ferroelectric materials that are opaque, the most outstanding feature of the PLZT materials is their high optical translucency and transparency. Optical transparency is both a function of the concentration of lanthanum and the Zr/Ti ratio with a maximum in transparency occurring along the FE-PE phase boundary and beyond, until mixed phases produce opacity (see Fig. 5). For example, the 65/35 Zr/Ti ratio compositions are most transparent in the lanthanum range from 8 to 16 at.%, whereas the 10/90 compositions are similarly transparent in the 22% to 28% range.

A typical transmission curve for a 9/65/35 composition is

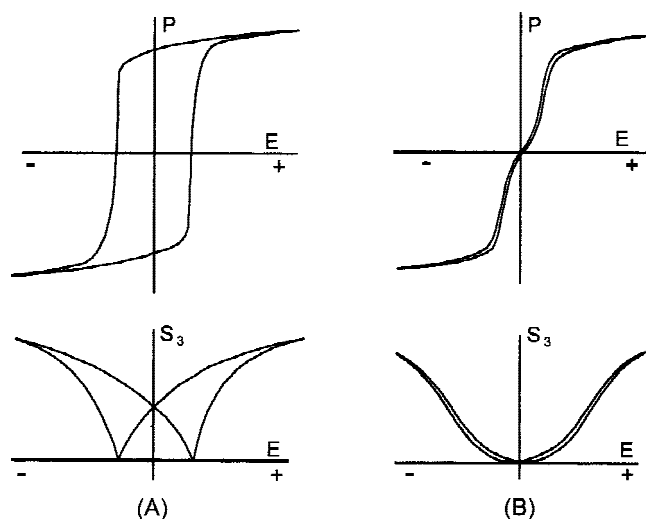


Fig. 12. Hysteresis loops and longitudinal strain curves for (A) ferroelectric memory ceramic and (B) SFE nonmemory relaxor ceramic.

given in Fig. 13. The material is highly absorbing below 0.37 μm , which is the commonly accepted value for the onset of high absorption in the bulk material. For thin films, this value is closer to 0.35 μm . A fairly constant optical transmission of $\sim 65\%$ occurs throughout the visible spectrum from 0.5 μm to the near infrared at 6.5 μm (see inset). Beyond this, absorption again begins to take place, and, at 12 μm , the material is, once again, fully absorbing. The high-surface-reflection losses ($\sim 31\%$ for two surfaces) shown in Fig. 13 are a function of the high index of refraction ($n = 2.5$) of the PLZT.

Four common types of electrooptic effects have been found to be operative in ferroelectric materials in general and in PLZT ceramics in particular: (1) quadratic, Kerr, and birefringent effects, (2) depolarization nonmemory scattering, (3) linear, Pockels, and birefringent effects, and (4) memory scattering. The first two types utilize relaxor-type, 9/65/35 materials with linearly polarized light; the third type uses a high coercive field, tetragonal, memory material, such as 12/40/60, with polarized light; and the fourth type commonly uses a low coercive field, rhombohedral, memory material, such as 7/65/35, and does not use polarizers, but, rather, relies on the variable-angle scattering of light from different polarized areas to achieve a spatially varying image in the ceramic. Contrast ratios as high as 3000/1 can be attained with polarized light, whereas these ratios are limited to $<50/1$ for schemes involving nonpolarized, scattered light. Specific properties of the more-common PLZT electrooptic compositions are listed in Table III.

PLZT materials are also known to possess many special photosensitive phenomena that are directly linked to their microstructural, chemical, electronic, and optical properties, including (1) photoconductivity, (2) photovoltaic properties, (3) photo-assisted domain switching, (4) ion-implantation-enhanced photosensitivity, (5) photochromic effects, (6) photomechanical (photostrictive) behavior, (7) photorefractive effects, and (8) photoexcited space charge phenomena.^{70,71} Although materials with such a multitude of properties and special effects hold promise for many new applications for the future, it should also be remembered that these same effects can, and often do, limit their application.

V. Applications

The applications for ferroelectric ceramics are manifold and pervasive, covering all areas of our workplaces, homes, and automobiles. Similar to most materials, the successful application of these piezoelectric, pyroelectric, ferroelectric, electrostrictive, and electrooptic ceramics and films are highly dependent on the relative ease with which they can be adapted to useful and reliable devices. This is, to a great extent, the reason that they have been so successful over the years in finding an increasing number of applications. Their simplicity, compact size, low cost, and high reliability are very attractive features to the design engineer. Many general category applications for bulk and film electroceramics are given in Fig. 14. As indicated in Fig. 14, some of these applications are more appropriate for bulk materials, some for films, and some for both bulk and films. Although there always will be a demand for bulk devices, it is certainly obvious that the trend in the industry is toward film devices. The reasons for this include (1) lower operating voltages, (2) size and weight compatibility with integration trends, (3) better processing compatibility with silicon technology, (4) ease of fabrication, and (5) lower costs through integration.

(1) Capacitors

One category of applications for ferroelectric-type materials is that of high-dielectric-constant capacitors, particularly 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. Most ceramic capacitors are, in reality, high-dielectric-constant ferroelectric compositions which have their ferroelectric (hysteresis loop) properties suppressed with suitable chemical dopants while retaining a high dielectric constant over a broad temperature range. BaTiO_3 was historically the first composition used for high-dielectric-constant capacitors, and it (or its variants) remains the industry standard; however, lead-containing relaxors such as PMN and PZN are making inroads.⁷² In tune with ever-shrinking electronic components in

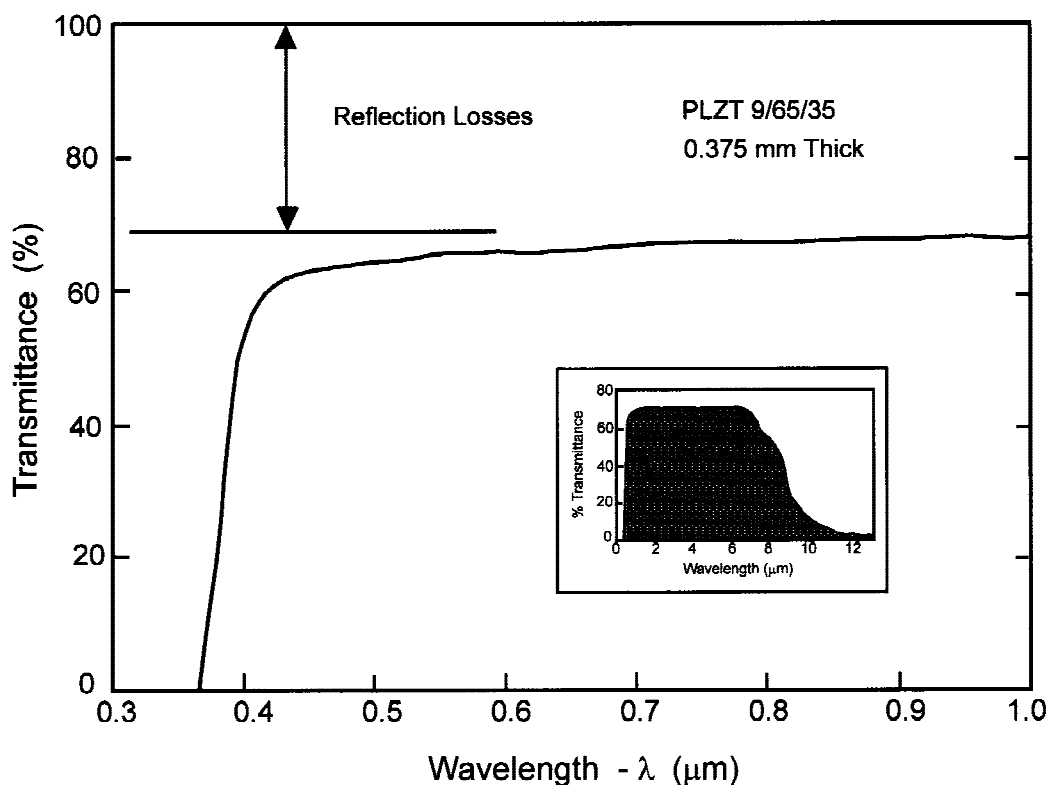


Fig. 13. Optical transmission characteristics of electrooptic PLZT (9/65/35).

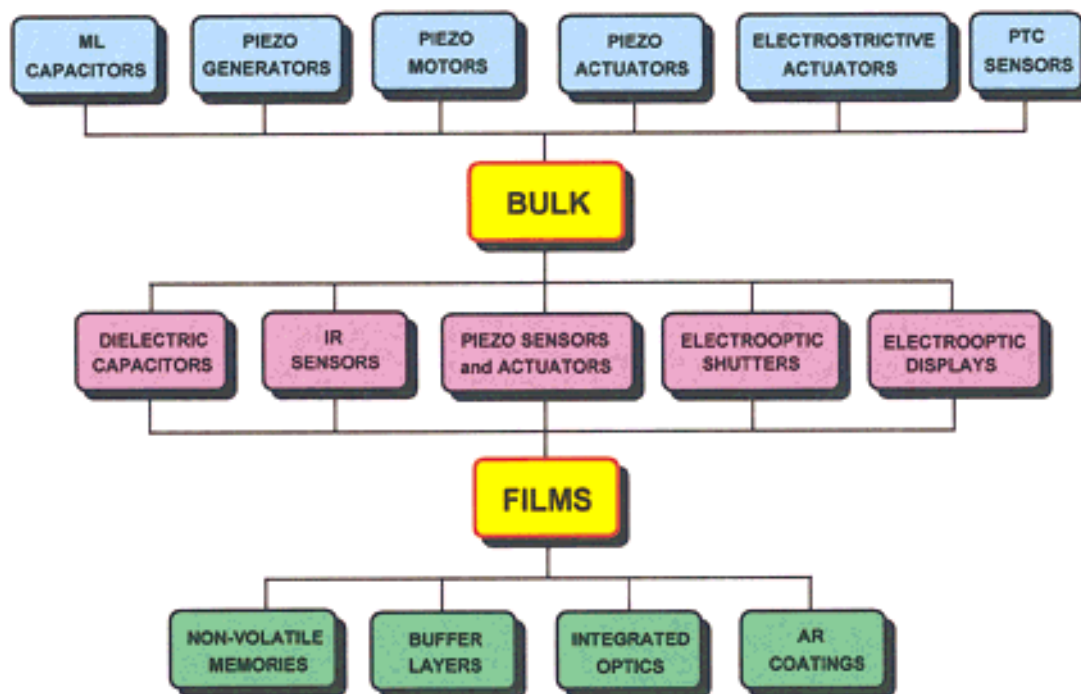


Fig. 14. Applications of bulk and film ceramic electronic materials.

this age of integration, capacitor techniques have trended toward (1) more-sophisticated tape-casting procedures, (2) surface-mount MLCs, and (3) fired layer thicknesses approaching 4 μm . MLCs, 0.5 mm \times 1 mm and several hundred layers thick, are now produced with capacitances of several microfarads. Tape-casting methods are now reaching their practical limit, and thin-film deposition techniques are being explored. Typical applications include general-use discrete and MLCs, voltage-variable capacitors, and energy-storage capacitors.^{28,40}

By far the largest majority of applications for electro-active materials occurs in the area of piezoelectric ceramics. In this category, the ceramics are usually poled once at the factory, and no polarization reorientation takes place after that throughout the life of the device. These devices can be divided into four different groups, as given in Fig. 15. Two of these groups are as mentioned previously, i.e., motors and generators; however, the third category involves the use of combined motor and generator functions in one device, and the fourth category includes devices operated at higher frequencies, i.e., at resonance. Because of the more-recent interest in electrically biased electrostrictive devices that act as electrically tunable piezoelectric components, some of the specific applications in Fig. 15 are also now being developed with electrostrictive materials. Examples of ceramics that are utilized in a variety of piezoelectric and electrostrictive applications, both large and small, are shown in Fig. 16.

Figure 15 also shows that the number of applications for piezoelectrics as motors is quite numerous. This is particularly true for the whole family of micro- and macro-piezoelectric actuators. The micro-devices are considered to be those that utilize the basic piezoelectric strain of the ceramic (measured in micrometers), whereas the macro-devices are those that use a displacement-amplifying mechanism to enhance the fundamental strain (measured in millimeters). This is explained more thoroughly in Table IV, which lists all of the current ceramic actuator technologies and includes some of their important characteristics. Table IV shows that a variety of direct extensional configurations, composite flexensional structures, and bending-mode devices are used to achieve a mechanical output. Maximum stress generation (40 MPa) or loading capability is noted for all of the direct extensional devices, including the piezoelectrics, electrostrictors, and antiferroelectrics; however,

their strain (displacement) is limited to $\sim 0.5\%$ or less. On the other hand, maximum displacement of several tens of percent can be achieved with displacement-amplifying means, such as composite (flexensional structure, Moonie) or bender (unimorph, bimorph, RAINBOW) structures, but this is usually accomplished at the expense of considerably less force generation, greater complexity, and higher cost. In most cases, the actuators are operated with electric fields < 10 kV/cm for long-levity and reliability. However, even such modest fields can result in rather high voltages (> 1000 V) if the actuator is relatively thick ($V = Et$); thus, the multilayer technology developed for capacitors is often used to reduce the operating voltage below 100 V.

Although unimorph and bimorph structures have been suc-

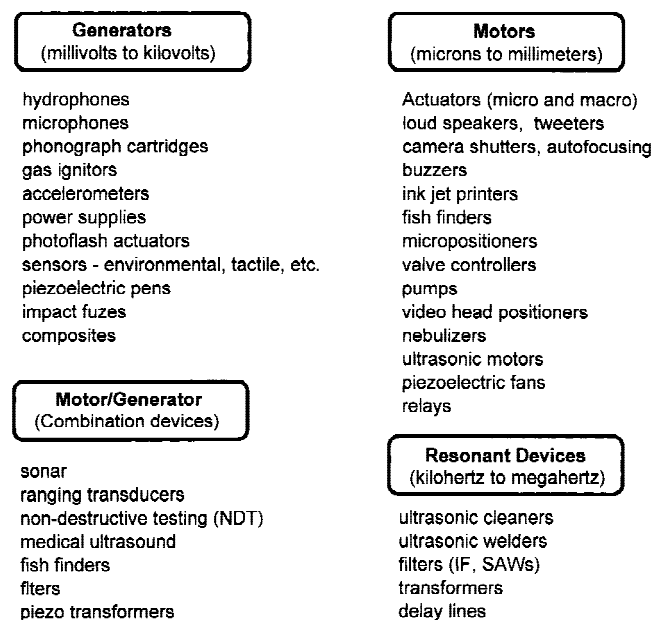


Fig. 15. Piezoelectric and electrostrictive applications for ferroelectric ceramics.

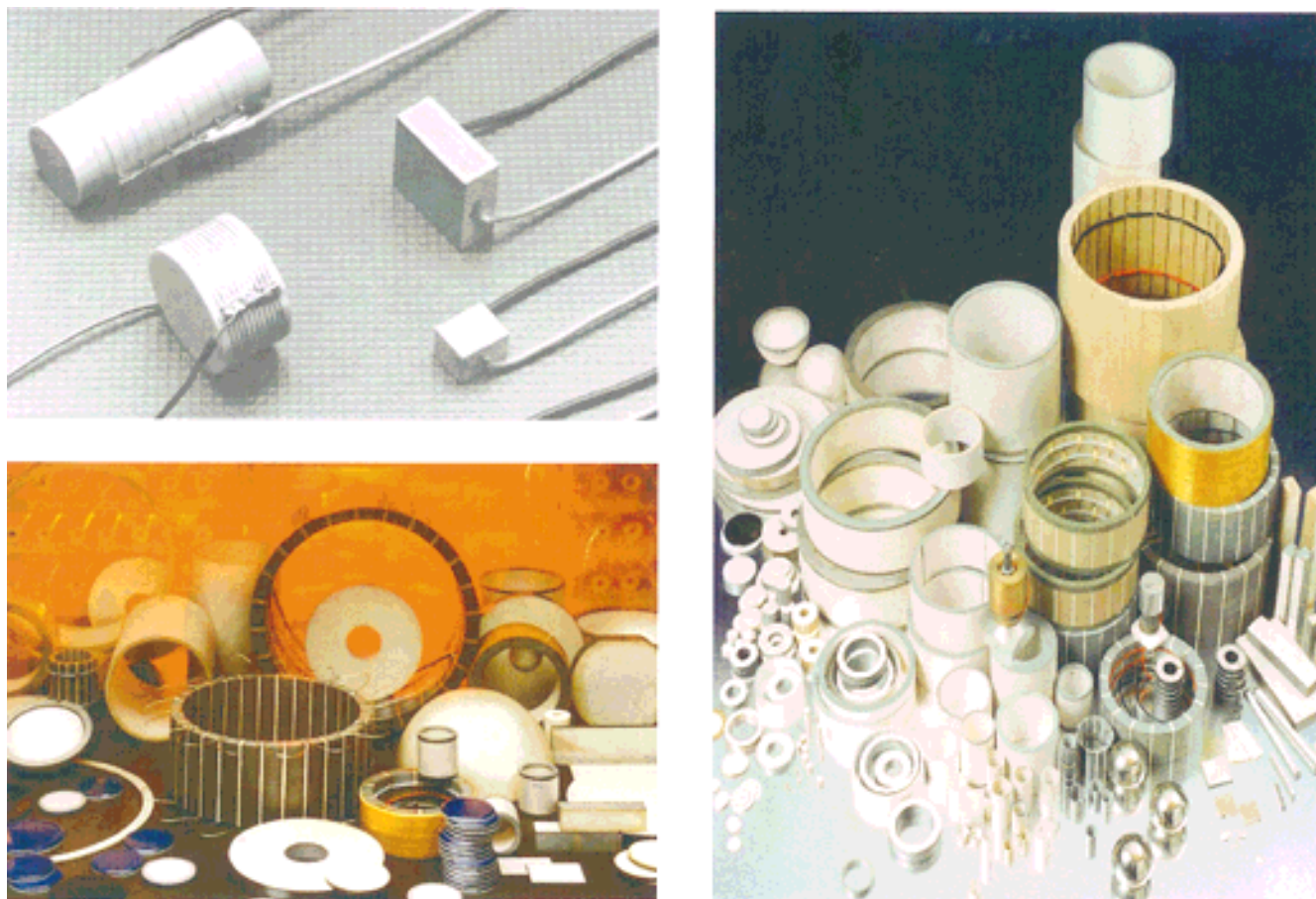


Fig. 16. Variety of ferroelectric ceramics used in piezoelectric and electrostrictive applications, such as sonar, accelerometers, actuators, and sensors. (Photograph courtesy of EDO Western.)

cessfully applied to many devices over the past four decades, their inability to extend the force–displacement envelope of performance has led to a search for new actuator technologies. One such device developed in the early 1990s is the Moonie—so named because of its crescent-shaped, shallow cavities on the interior surfaces of the end caps (see Table IV), which are bonded to a conventionally electroded piezoelectric ceramic disk. When the ceramic is activated electrically, the shallow cavities permit the end caps to flex, thus converting and amplifying the radial displacement of the ceramic into a large axial motion at the center of the end caps. Advantages of the Moonie include (1) a factor of 10 enhancement of the longitudinal displacement, (2) an unusually large d_{33} coefficient exceeding 2500 pC/N, and (3) enhanced hydrostatic response.^{73,74} Recent improvements in the basic Moonie design have resulted in an element called a Cymbal, a device that possesses more-flexible end caps, resulting in higher displacement.⁷⁵ Applications include transducer arrays, medical imaging transducers, and hydrophones.

Another device recently developed to increase the force–displacement performance of a piezoelectric actuator is the RAINBOW. In its most basic sense, a RAINBOW can be thought of as a prestressed, axial-mode bender similar in operation to the more conventional unimorph bender. Unlike the unimorph and Moonie, which are composite structures, the RAINBOW is a monolithic monomorph that is produced from a conventional, high-lead-containing piezoelectric ceramic by means of a high-temperature, chemical reduction reaction. As mentioned previously, this process produces significant internal compressive and tensile stresses that are instrumental in achieving its unusually high displacement characteristics. Displacements as high as 0.25 mm for a 32 mm diameter \times 0.5 mm thick wafer have been achieved for these devices in a dome

mode of operation while sustaining loads of 1 kg. Maximum displacements of >1 mm can be achieved with wafers (32 mm diameter), thinner than 0.25 mm when operating in a saddle mode. Prototypes of RAINBOW pumps, speakers, optical deflectors, vibratory feeders, relays, hydrophones, switches, platform levelers, sensor and actuator arrays, and toys have been demonstrated; however, no commercial products have been yet been produced.^{53,76} Some examples of these different types of piezoelectric devices are included in Fig. 17.

A novel type of bimorph application of somewhat recent vintage is the optomechanical (photostrictive) actuator. The photostrictive behavior is a result of a combined photovoltaic effect (wherein light produces a voltage in the ceramic) and a piezoelectric effect (wherein this voltage produces a strain in the material via the converse piezoelectric effect). PLZT ceramics with donor-type doping exhibit large photostrictive effects when irradiated with high-energy, near-ultraviolet light. A bimorph configuration with no connecting wires has been used to demonstrate prototypes of a photo-driven relay and a remote micro-walking device, and a photophone of the future has been envisioned.^{77,78}

(2) Explosive-to-Electrical Transducers (EETs)

Studies on the stress-induced depoling of ferroelectric ceramics were initiated in the mid-1950s, which culminated in the development of one-shot power supplies that made use of this effect. This depoling behavior is optimum (i.e., maximum output in the shortest period of time) for ferroelectric compositions located along the boundary between the polar ferroelectric phase and the nonpolar antiferroelectric phase, such as shown in the gray area of the phase diagram of Fig. 5. Although this depoling does occur somewhat more slowly under hydrostatic pressure, when it is accomplished in an extremely fast

Table IV. Current Ceramic-Actuator Technologies

Type	Configuration [†]	Maximum stress generated (MPa)	Actuator movement (with voltage applied)	Actuator type [‡]	Actuator displacement (%) [§]
Monolithic (d_{33} mode)		40	Expansion	P	0.40
Monolithic (d_{31} mode)		40	Contraction	P	-0.15
Monolithic (s_{11} mode)		40	Expansion	E	0.28
Monolithic (s_{12} mode)		40	Contraction	E	-0.09
Monolithic (s_{11} mode)		40	Expansion	A	0.50
Monolithic (s_{12} mode)		40	Expansion	A	0.08
Composite structure (d_{33} mode) (flextensional)		10	Contraction	P/E	-1.0
Composite structure (d_{33}/d_{31}) (Moonie)		0.028	Expansion	P/E	1.3
Unimorph (bender)		0.006	Expansion/contraction	P/E	10
Bimorph (bender)		0.006	Expansion/contraction	P/E	20
Rainbow monomorph (bender)		0.02	Expansion/contraction	P/E/A	35 (<i>D</i>) 450 (<i>S</i>)

[†]V is voltage and D is actuator displacement. [‡]P is piezoelectric, E is electrostrictor, and A is antiferroelectric. [§]D is dome mode and S is saddle mode; displacement at ± 10 kV/cm based on thickness.

mode via explosive shock waves or projective impact, useful electrical pulses of a few hundred kilovolts or kiloamps lasting for many microseconds can be obtained. These one-shot power supplies have found many uses in military applications.^{79,80}

(3) Composites

Piezoelectric composites represent one of the latest technologies developed for engineering the last bit of high performance from a piezoelectric transducer. When one deliberately introduces a second phase in a material, connectivity of the phases is a critical parameter. There are 10 connectivity patterns possible in a two-phase solid, ranging from 0-0 (unconnected three-dimensional checkerboard pattern) to 3-3 (interpenetrat-

ing pattern in which both phases are three-dimensionally self-connected). Some of these connectivity patterns are particularly well suited for decoupling the longitudinal and transverse piezoelectric effects, such that materials with significantly enhanced (up to a factor of 100 or more) piezoelectric properties are possible. Moreover, a ceramic-polymer composite offers distinct advantages, such as a wide range of acoustic impedance matching, broad bandwidth, low electrical losses, and, for medical ultrasound applications, send-receive capability in a compact package. Considerable engineering ingenuity has been demonstrated in designing, fabricating, and packaging the many types of diphasic structures. Major applications include hydrophones, sensors, and medical ultrasonics.⁸¹⁻⁸⁴



Fig. 17. Examples of PZT, PLZT, and PMN piezoelectric and electrostrictive devices: (starting at upper right and going clockwise) Motorola tweeter, Triangle gas-grill lighter, Motorola bimorph, Murata intermediate frequency resonators, Morgan Matroc ultrasonic cleaner ceramics, Aura RAINBOW ceramics, Itek PMN actuator, ferroelectric film memory, Kodak PLZT E/O device, RAINBOW mouse toy actuator, Moonie actuators, Radio Shack buzzer, and unimorphs.

(4) Electrooptics

Since the late 1960s, when transparent PLZT materials were first developed, ferroelectric ceramics have been thoroughly researched, and their characteristics studied to the point that they have now taken their place alongside single crystals as legitimate candidates for electrooptic applications. Compared to single crystals, ferroelectric ceramics are generally, but not always, less transparent, less uniform on a microscopic scale because of their polycrystalline nature, and somewhat less optimum in their electrooptic and hysteretic properties. On the other hand, electrooptic ceramics have several specific characteristics that make them well suited for a variety of electrooptic applications. Among these characteristics are (1) small areas (on the order of the grain size, from 1 to 10 μm) that can be electrically switched independently of other adjacent areas, (2) switched areas that are stable with time in memory materials or stable with applied electric field in nonmemory materials, (3) light transmission characteristics of the switched areas that depend on the thoroughness and direction of switching or poling, (4) switched areas that exhibit either electrically variable light scattering behavior or electrically variable birefringence, and (5) ceramics that can be hot-pressed or sintered in a variety of sizes and shapes with a high degree of optical uniformity on a macroscopic scale.

Thin polished plates of PLZT, such as 9/65/35, when used in conjunction with linearly polarized light, make excellent wide-aperture electrooptic shutters, linear gate arrays, and color filters. Their fast response (in the low microsecond range), thin profile, wide viewing angle, and wide temperature range of operation (-40°C to $+80^\circ\text{C}$) are highly desirable characteristics for most devices; however, these are offset by the disadvantages of (1) low ON-state transmission of $\sim 15\%$ as a result of the polarizers and (2) high operating voltages (~ 350 V) that are required to reach a full ON condition. Despite the low ON-state transmission characteristics, high contrast ratios of 3000/1 are easily achieved when high-efficiency polarizers are used.

The polarizer-PLZT configuration usually used in a shutter device is shown in Fig. 4. Vacuum-deposited or grooved, interdigital electrodes (not shown) are commonly used to decrease the operating voltage by reducing the gap between the positive and negative finger electrodes. These finger electrodes are thin enough (<0.075 mm) so that they can be optically defocused and the imaging preserved. Such an arrangement is used in the eye-protective systems developed by the military, in linear light gate arrays for printers and processors, and in seg-

mented transmissive and reflective displays.^{27,34} Several commercial and military applications for PLZT shutters and linear gate arrays are given in Fig. 18.

(5) Films

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 developed and is steadily increasing in intensity. Aside from the obvious advantages, such as smaller size, less weight, and easier integration to IC technology, ferroelectric films offer additional benefits, including (1) lower operating voltage, (2) higher speed, and (3) the ability to fabricate unique micro-level structures. Equally important, but not as obvious, is the fact that many materials that are difficult, if not impossible, to fabricate to a dense ceramic as a bulk material are relatively easy to produce as films. Moreover, the sintering temperatures of the films are usually hundreds of degrees celsius lower than that of the bulk, and this often can be the deciding factor in a successful design and application.^{57,59-61}

The several most important film applications are included in Fig. 14. Here again, some applications are exclusively designated for films while others are mutually shared with bulk materials. Applications for thick films (2–20 μm) include electrooptic and some piezoelectric devices, whereas the remaining applications (i.e., capacitors, infrared sensors, memories, buffer layers, integrated optics, and antireflection coatings) involve thin films ranging in thickness from 0.2 to 2 μm .⁸⁵ The reason for the thicker films in the former cases is to obtain maximum strain or electrooptic output from the films without having to resort to electric fields too near to dielectric breakdown.⁸⁶ This is not a problem in the latter applications, because the films are subjected only to low voltages (<10 V) or to no voltage in their operational environment.

Large-scale manufacturing is presently underway to incorporate ferroelectric films as storage and bypass capacitors in and other IC circuitry. In a conventional DRAM (dynamic random-access memory) computer memory application, one SiO_2 capacitor is in series with every switching transistor; however, as the memories become more dense, the area taken up by the low-dielectric-constant SiO_2 capacitor is too large, and new materials with higher dielectric constants must be substituted. A ferroelectric DRAM (FEDRAM) film, because of its much higher dielectric constant (~ 1000 vs 4), 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.⁵⁹ As memories become more dense 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. At present, BST film capacitors are the top contenders for these applications.

The development of ferroelectric random access memory (FERRAM) films for nonvolatile memory applications, such as computer random-access memories, smart cards, and radio-frequency identification tags, is presently underway and has reached modest production levels for specific niche applications.⁵⁹ The issues faced in nonvolatile memories are much more challenging than those involving simple capacitors, because, in the nonvolatile case, the two memory states consist of the two polarization states (polarization up and polarization down in Fig. 3) in the film, one being a 0 and the other being a 1. In this case, the ferroelectric polarization is constantly being switched, and this immediately raises the issue of switching fatigue. FERRAM films of several compositions, including PZT, PLZT, and $\text{SrBi}_2\text{Ta}_2\text{O}_7$ (SBT is a layer-type ferroelectric, see Table II), are actively being investigated. Among these, SBT is, perhaps, the material of choice in regard to fatigue. SBT materials exhibiting little ($<10\%$) fatigue out to 10^{12} switching cycles have been developed; however, this value must be increased to $\sim 10^{14}$ cycles before these films can be used in large-scale applications. Electrode-ceramic interac-

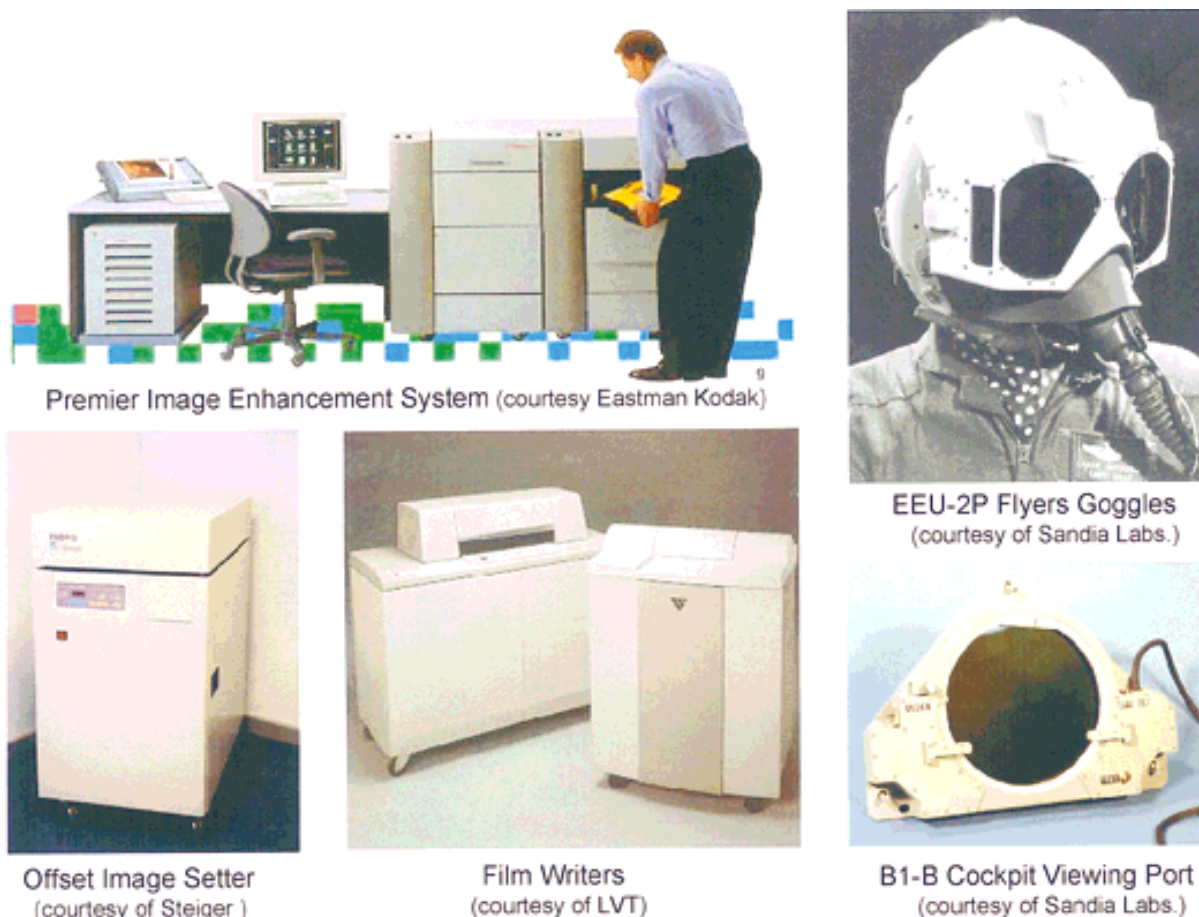


Fig. 18. Commercial and military applications of PLZT electrooptic ceramics: (starting at upper right and going clockwise) EEU-2P flyers goggles (Photograph courtesy of Sandia National Laboratories.), B1-B cockpit viewing port (Photograph courtesy of Sandia National Laboratories.), film writers (Photograph courtesy of LVT.), offset image setter (Photograph courtesy of Steiger.), and premier image enhancement system (Photograph courtesy of Eastman Kodak.).

tions, resistance degradation, and memory imprint (persistent memory, i.e., the resistance to switch out of a given memory state) also have been identified as major problems in these materials, and satisfactory solutions to these issues are critical to their success.

VI. Future Prospects

Present market trends continue to show that the future for ferroelectric ceramics is bright and continues to get even brighter as the transition is made from passive to electrically active “smart” and “very smart” materials. In this regard, a smart material senses a change in the environment and, using an external feedback control system, makes a useful response, as in a combined sensor/actuator ceramic. A very smart material senses a change in the environment and responds by reacting and tuning (self-controlling) one or more of its properties to optimize its behavior. An example of the smart type is a piezoelectric ceramic and of the very smart type is a nonlinear, electrostrictive relaxor. Multifunctionality is a key concept of these materials that will be exploited with all the ingenuity that design engineers can muster.⁸⁷

In the future, more and more applications for nonlinear, electrostrictive relaxor materials, such as PMN and PLZT, will emerge as the relentless drive toward miniaturization and integration continues. Indeed, this very trend will also encourage more materials research efforts to develop better ferroelectric and electrostrictive ceramics.

As niche applications become more prevalent in the future,

composites and displacement-amplifying techniques and materials will proliferate in a continuing effort to widen the force-displacement envelope of performance. These devices, too, will become smarter and smarter as the applications demand.

Brought on by the need for higher-capacity memories, expanded data processing capability, and smarter devices, the direction set a few years ago for ferroelectric films is expected to continue and broaden in scope. Thin- and thick-film technologies alike will also share in the current trend toward composite and graded structures with specifically engineered, and often unique, properties. Multiply deposited layers of different materials, or graded layers of the same material, are now achievable with most conventional film deposition processes on a micro scale, and this will be more commonplace in the future on a nano scale.^{88–91}

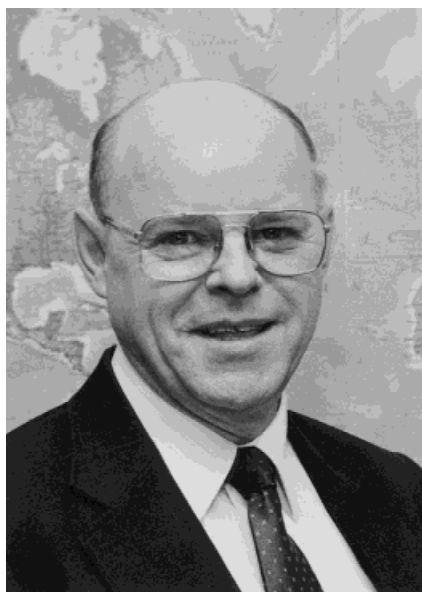
Because thin- and thick-film technologies generally do not limit, but rather enhance, the portfolio of materials to be used in various applications, it is expected that a variety of materials will continue to be studied, but there will be a narrowing down to fewer serious candidates of known behavior in order to bring the devices in development to the marketplace. Undoubtedly, BST, PZT, PLZT, PMN, and SBT are destined to be leading candidates in this arena. Regarding film deposition techniques, at this stage in the development of the films, it is very difficult to judge which film deposition technique will emerge as the favorite; however, because several methods have been used successfully, it is most likely that several methods will survive, and a specific method selected will be dictated by cost and the application.

Because of their intrinsic dielectric nature and large number of interactive and electrically variable properties, ferroelectric ceramics are destined to figure prominently in the future. Bulk, thick-film, and thin-film forms of these materials have now proved their worth, and, together, they will constitute a strong portfolio of materials for future applications in electronics.

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Gene Haertling received his B.S. degree in ceramic engineering from the University of Missouri at Rolla in 1954. His M.S. and Ph.D. degrees, also in ceramic engineering, were earned from the University of Illinois in 1960 and 1961, respectively. From 1961 to 1973, he held staff and managerial positions at Sandia National Laboratories. During this time he developed the first transparent ferroelectric ceramics, the PLZT (lead lanthanum zirconate titanate) materials, which are now used in both military and commercial applications. From 1974 to 1987, he was Vice-President of the Technical Staff and Manager of the Ceramic Research Group at Motorola, Inc., Albuquerque, NM. Just prior to joining Motorola, he was president of Optoceram, Inc., a small entrepreneurial company he founded, which was engaged in the development and manufacture of PLZT electrooptic ceramics. After briefly serving on the faculty at University of Missouri at Rolla from 1987 to 1988, Dr. Haertling joined the Ceramic Department of Clemson University as the Bishop Distinguished Professor of Ceramic Processing. While at Clemson, he developed the special process for producing high-displacement, piezoelectric ceramic actuators known as RAINBOWS. He is a member of the National Academy of Engineers and a Fellow of The American Ceramic Society and the IEEE. He has published 85 technical papers, 3 book chapters, and is a coholder of 10 patents in the area of ferroelectric and electrooptic ceramic materials and devices. Recently retired from active teaching, Dr. Haertling is Professor Emeritus of Clemson University and is presently located in Albuquerque, NM.