31

Locally Redistributing Charge

CHAPTER PREVIEW

In this chapter, we describe ceramic dielectrics. A dielectric is by definition an electrical insulator (ρ is high, E_g is large). That means that dielectric behavior is a property associated with certain ceramics and polymers but not a property associated with metals. We begin with a background section. You may have covered some of this material before but perhaps not thinking specifically of ceramics.

Dielectrics in the context of this chapter are more than just passive insulators. For example, in $BaTiO_3$ and related perovskites, structural changes create permanent electric dipoles that cause the material to become polarized. Polarization allows, among other things, the material to store large amounts of charge: a prerequisite for a capacitor. Without dielectrics, computers can't function; some of today's biggest challenges for the electronics industry concern dielectrics more so than the semiconductor.

The key topics in this chapter are:

- Dielectrics are polarizable: the separated charges cause an electric field that we characterize by the dielectric constant.
- Dielectrics can be self-polarizing: this is the ferroelectric effect. These ceramics are used in capacitors because of their high dielectric constant.
- The dimensions of a dielectric may change when it is polarized: this is the piezoelectric effect and is used in micro-electro-mechanical systems (MEMS), sonar, and medical ultrasound imaging.
- The spontaneous polarization of a dielectric depends strongly on temperature; this is the pyroelectric effect that we use for infrared (IR) detection (e.g., intruder alarms, thermal imaging).

31.1 BACKGROUND ON DIELECTRICS

All materials contain electrically charged particles. At a minimum, these are the electrons and protons that are part of the constituent atoms. Many ceramics also contain ions, which are charged. In a dielectric, charges have limited mobility, and they move only when they have enough energy to overcome their inertia. When an insulator receives a charge, it retains that charge, confining it within the localized region in which it was introduced. On the other hand, a conductor allows charge to flow freely and redistribute itself within the material. The distinction between conductors and nonconductors (and it's not always a clear one) arises from the relative mobility of charge within the material.

The terms "dielectric," "nonconductor," and "insulator" are often used interchangeably, although we often specify dielectrics as materials that are not only electrically insulating but also have a high dielectric constant, κ.

Table 31.1 lists the important parameters we meet in this chapter and their units.

31.1.1 Polarization Mechanisms

Even though no charge is transferred when a dielectric is placed in an electric field there is a redistribution of charge, which occurs by the formation and movement of electric dipoles. There is an associated dipole moment, μ, having both magnitude and direction:

$$\mu = qd \tag{31.1}$$

where d is the separation of the positive and negative ends of the dipole. The dipole direction is, by convention, taken to point from the negative end to the positive end.

When a dielectric material is placed in an electric field, the induced dipoles and any permanent dipoles become

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TABLE 31.1 Terms and Units Used to Describe Dielectric Behavior

Parameter	*Definition*	*Units/value*	*Conversion factor*
C	Capacitance	F, farads	$1\ F = 1\ C/V = 1\ A^2\ s^4\ kg^{-1}\ m^{-2}$
ε_0	Permittivity of a vacuum	8.85×10^{-12} F/m	
ε	Permittivity	F/m	
ε_r	Relative permittivity ($\varepsilon/\varepsilon_o$)	Dimensionless	
κ (same as ε_r)	Dielectric constant	Dimensionless	
P	Polarization	C/m^2	
Q	Charge	C, coulombs	$1\ C = 1\ A\ s$
μ	Dipole moment	C.m	
V	Voltage	V	
q or e	Electron charge	0.16 aC	
D	Dielectric displacement	C/m^2	$D = Q/A$
θ_c	Curie temperature	K	$0\ K = -273°C$
T_{cw}	Curie-Weiss temperature	K	
E_c	Coercive field	V/m	
χ	Dielectric susceptibility	Dimensionless	
ξ	Electric field strength	V/m	
C	Curie constant	K	

aligned. The material is now polarized, and the polarization (or dipole moment per unit volume) is given by:

$$P = Nqd \tag{31.2}$$

where N is the number of dipoles.

There are four possible polarization mechanisms in a dielectric.

- Electronic
- Ionic
- Dipolar (also called molecular or orientation)
- Interfacial (also called space charge)

These mechanisms are each illustrated in Figure 31.1.

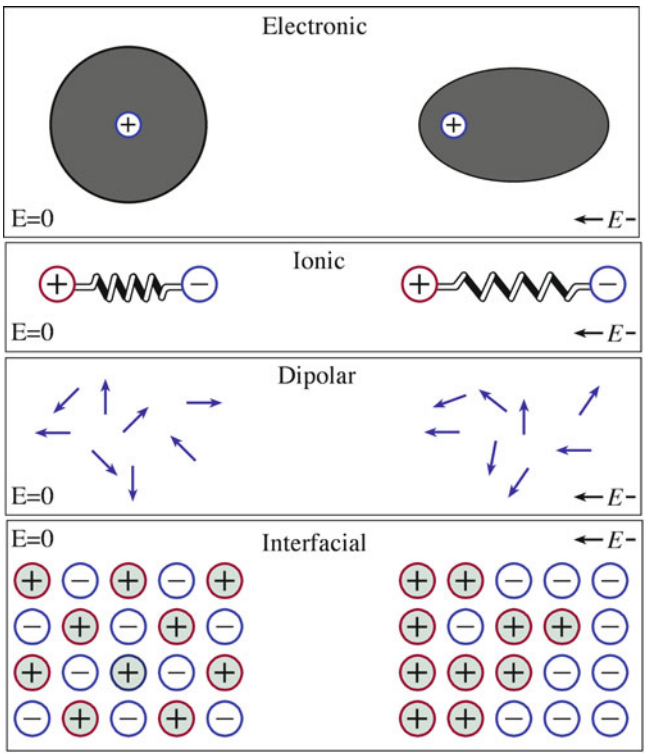


FIGURE 31.1. Different polarization mechanisms in a solid.

31.1.1.1 Electronic

When an electric field is applied to an atom, there is displacement of the electrons relative to the nucleus. The electrons concentrate on the side of the nucleus near the positive end of the field. The atom acts as a temporarily induced dipole. This effect occurs in all materials (because all materials contain atoms), but the magnitude is small because d is very small. Typical displacements are ~1 am, giving $\mu \sim 1.6 \times 10^{-37}$ C.m. Electronic polarization is the only possible mechanism in pure materials that are covalently bonded and do not contain permanent dipoles (e.g., diamond, silicon).

31.1.1.2 Ionic

Ionic polarization, which occurs when an ionically bonded material is placed in an electric field, is common in many ceramics (e.g., MgO, Al_2O_3, NaCl). The bonds between the ions are elastically deformed. Consequently, the charge is minutely redistributed. Depending on the direction of the field, the cations and anions move either closer together or farther apart. These temporarily induced dipoles cause polarization and may also change the overall dimensions of the material. The dipole moment is usually small because, once again, the displacements involved are very small. Typically, the ion displacements are only 10–100 am.

31.1.1.3 Dipolar

Dipolar polarization is generally uncommon in ceramics because most of the permanent dipoles cannot be reoriented without destroying the crystal structure. However, there are some very important exceptions, and it is these materials that form a large part of this chapter. The prototypical example is barium titanate, whose structure is shown in Figure 7.2. At room temperature, the octahedrally coordinated Ti^{4+} ion is displaced slightly from its ideal symmetric position, causing the crystal structure to become tetragonal and permanently polarized. When an alternating electric field is applied to a crystal of barium titanate, the Ti^{4+} ion moves back and forth between its two allowable positions to ensure that the polarization is aligned with the field.

POLARIZATION MECHANISMS

A note: In some texts you'll find that the polarization mechanism occurring in $BaTiO_3$ is described as dipolar in others as ionic. We prefer the former because $BaTiO_3$ contains permanent dipoles (a condition of dipolar polarization) that are being oriented in an electric field. Although the permanent dipoles in $BaTiO_3$ are the result of ion displacements, the term ionic polarization refers to the movement of any ions in an electric field (whether the material has a permanent dipole or not).

31.1.1.4 Interfacial

A charge may develop at interfaces (e.g., grain or phase boundaries and free surfaces) normally as a result of the presence of impurities. The charge moves on the surface when the material is placed in an electric field. This type of polarization is not well understood, although it has considerable practical interest because most real materials and, in particular, many ceramics are not pure.

The total P for the material is then the sum of all the individual contributions:

$$P = P_{\text{electronic}} + P_{\text{ionic}} + P_{\text{dipolar}} + P_{\text{interfacial}} \tag{31.3}$$

31.1.2 Relating *P* and *κ*

The dielectric constant is an important materials property. It is a measure of the ability of an insulating material to store charge when subjected to an electric field. As you might expect, it is directly related to P.

We can develop an equation relating P and κ by beginning with a simple parallel plate capacitor. From electromagnetic theory we know that the total charge per unit area of capacitor plate, D_0, is proportional to the applied electric field ξ. The constant of proportionality is ε_0.

$$D_0 = Q/A = \varepsilon_0 \xi \tag{31.4}$$

If we now place a dielectric between the parallel plates we write:

$$D = \varepsilon \xi \tag{31.5}$$

where D is also known as the dielectric displacement and represents the extra charge that can be stored because of the presence of the dielectric. Therefore, we can rewrite equation 31.5 as:

$$D = \varepsilon_0 \xi + P \tag{31.6}$$

By substituting equation 31.5 into equation 31.6, we obtain:

$$\varepsilon \xi = \varepsilon_0 \xi + P \tag{31.7}$$

By simple rearrangement we can write:

$$P = (\kappa - 1)\varepsilon_o \xi = \chi \varepsilon_o \xi \tag{31.8}$$

χ is a measure of the ratio of the bound charge/free charge (i.e., P/Q). For dielectrics that polarize easily, κ is large; and, in turn, a large quantity of charge can be stored.

Table 31.2 lists κ for a range of materials. Many ceramics and glasses have κ in the range of 4–10. Polarization is electronic only in covalent ceramics (e.g., diamond) and is a combination of electronic and ionic in

TABLE 31.2 Dielectric Constants of Various Ceramics

Material	*κ at 1 MHz*	*Material*	*κ at 1 MHz*
Diamond	5.5–6.6	Al_2O_3	8.8
SiO_2	3.7–3.8	MgO	9.6
NaCl	5.9	$BaTiO_3$	3,000
Mica	5.4–8.7	Pyrex glass	4.0–6.0
Soda-lime glass	7.0–7.6	TiO_2	14–110
Steatite (SiO_2 + MgO + Al_2O_3)	5.5–7.5	Forsterite (2MgO.SiO_2)	6.2
Cordierite (SiO_2 + MgO + Al_2O_3)	4.5–5.4	Mullite	6.6
High-lead glass	19	Vycor glass	3.9

materials such as MgO. Some ceramics, in particular $BaTiO_3$ and other titanates and zirconates, have very large κ due to their permanent dipole moments.

31.1.3 Frequency Dependence of Polarization

When a dielectric is placed in an alternating electric field, the dipoles attempt to maintain alignment with the field. This process requires a finite time, which is different for each polarization mechanism. At the relaxation frequency, the dipoles are only just able to reorient themselves in time with the applied field. At this frequency, the dielectic is "lossy," and energy is lost in the form of heat. The dielectric loss is maximum when the frequency of the external field coincides with the relaxation frequency of a given polarization mechanism. This is the principle behind the microwave oven. We operate at the relaxation frequency of water molecules, and the heat generated warms the food.

At frequencies above the relaxation frequency, the dipoles are no longer able to keep up with changes in the applied field. The contributing polarization mechanism becomes effectively "frozen" and no longer contributes. Figure 31.2 shows the variation of polarization with frequency for a hypothetical material that exhibits all of the four polarization mechanisms.

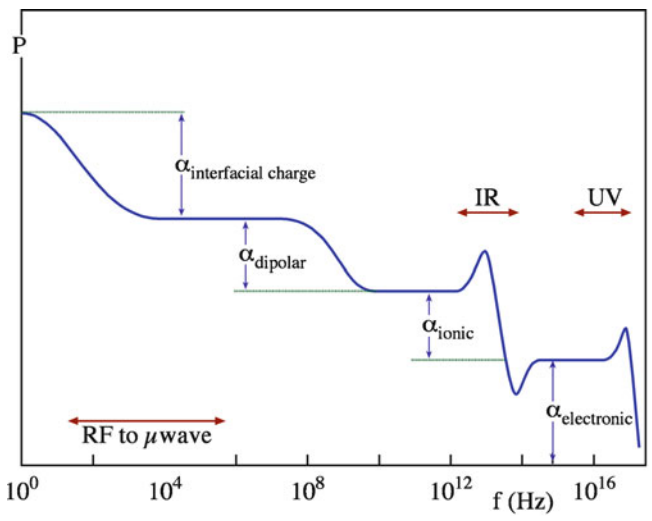


FIGURE 31.2. Frequency dependence of polarization.

REAL AND IMAGINARY COMPONENTS OF ε

The permittivity under an alternating field can be represented mathematically as the sum of real (ε') and imaginary (ε'') parts

$$\varepsilon = \varepsilon' - j\varepsilon'' \qquad \text{(B1)}$$

In an alternating electric field the phase angle of the electric flux density lags behind that of the electric field due to the finite speed of polarization. The delay angle δ is

$$\tan\delta = \varepsilon''/\varepsilon' \qquad \text{(B2)}$$

The electric power loss per unit time (also called the dielectric loss) is proportional to tan δ. Typical values are given in Table 31.3.

- At optical frequencies, only electronic polarization is operative.
- Dipolar and ionic contributions are small at high frequencies because of the inertia of the molecules and ions. The peaks occurring at ~10^{13} and ~10^{15} Hz are due to resonance effects, where the external field is alternating at the natural vibrational frequency of the bound ions or electrons, respectively.

31.1.4 Dielectric Strength

A dielectric is able to withstand a certain applied electric field strength before it breaks down and current flows. High dielectric strengths are important in applications where the thickness of the material is small (e.g., in capacitors). Values of dielectric strength for several ceramics are given in Table 31.4. Note the very high value of mica—one of the reasons it was used in early ceramic disk capacitors.

31.1.5 Nonlinear Dielectrics

Nonlinear dielectrics have permanent dipoles that interact to give polarization in the absence of an applied electric field. These materials are the ferroelectrics. The topic

TABLE 31.3 Dielectric Loss for Some Ceramics and Glasses at 25°C and 1 MHz

Material	*Tan δ*
LiF	0.0002
MgO	0.0003
KBr	0.0002
NaCl	0.0002
TiO_2 (ll c)	0.0016
TiO_2 (ll a,b)	0.0002
Al_2O_3 (ll c)	0.0010
Al_2O_3 (ll a,b)	0.0010
BaO	0.0010
KCl	0.0001
Diamond	0.0002
Mg_2SiO_4 (forsterite)	0.0003
Fused silica glass	0.0001
Vycor ($96SiO_2$–$4B_2O_3$) glass	0.0008
Soda-lime silica glass	0.0100
High-lead silica glass	0.0057

TABLE 31.4 Dielectric Strengths for Various Ceramics

Material	*Dielectric Strength (MV/cm at 25° C)*
Al_2O_3 (99.5%)	0.18
Al_2O_3 (94.0%)	0.26
High-voltage porcelain	0.15
Steatite porcelain	0.10
Lead glass	0.25
Lime glass	2.5
Borosilicate glass	5.8
Fused quartz	6.6
Quartz crystal	6.0
NaCl [100], [111], [110]	2.5, 2.2, 2.0
Muscovite mica	10.1

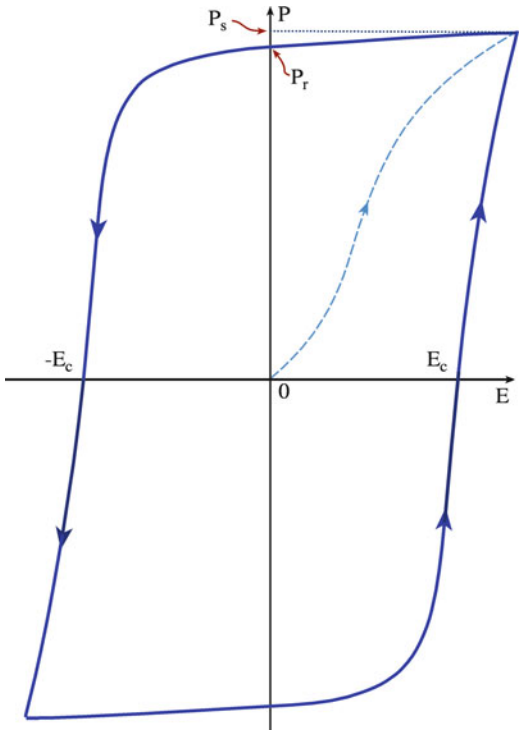


FIGURE 31.3. Hysteresis curve for a typical ferroelectric.

shares many similarities with ferromagnetism, described in Chapter 33. For example, above a critical temperature, the Curie temperature θ_c, the spontaneous polarization is destroyed by thermal disorder. A plot of P versus ξ is shown in Figure 31.3 and demonstrates hysteresis. This behavior is similar to that produced by a ferromagnet when it is cycled through an alternating magnetic field. The description is based on the domain structure of ferroelectrics.

When the dipoles in a crystal are randomly oriented, there is no net P. When a field is applied, the dipoles begin to line up with the electric field. The total dipole moment changes either by the movement of the walls between domains or by the nucleation of new domains. Eventually, the field aligns all of the dipoles, and P_s is obtained. When all the dipoles are aligned in the same direction, the material is "poled."

When the field is subsequently removed, a remnant polarization P_r exists due to the coupling between adjacent dipoles. The material is permanently polarized in the absence of an electric field. This property is key to ferroelectricity.

When the direction of ξ is reversed, the dipole orientation switches to become aligned with the new field direction. As the strength of the reverse field is increased, P_s eventually occurs with the opposite polarization. As the field alternates, a hysteresis loop is produced. The area contained within the loop is related to the energy required to cause the polarization to switch directions. Linear dielectrics (which is most of them) do not show significant hysteresis in an alternating electric field.

TABLE 31.5 Noncentrosymmetric Crystals

Crystal system	*Noncentrosymmetric point groups*	*Piezoelectric*	*Pyroelectric*
Triclinic	1	Yes	Yes
Monoclinic	2	Yes	Yes
	m	Yes	Yes
Orthorhombic	mm2	Yes	Yes
	222	Yes	No
Tetragonal	4	Yes	Yes
	$\bar{4}$	Yes	No
	422	Yes	No
	4mm	Yes	Yes
	$\bar{4}$2m	Yes	No
Trigonal	3	Yes	Yes
	32	Yes	No
	3m	Yes	Yes
Hexagonal	6	Yes	Yes
	$\bar{6}$	Yes	No
	622	Yes	No
	6mm	Yes	Yes
	$\bar{6}$m2	Yes	No
Cubic	23	Yes	No
	432	No	No
	$\bar{4}$3m	Yes	No

There is a structural requirement for ferroelectricity. There are a total of 32 different symmetry point groups, 21 of which do not possess a center of symmetry. Ferroelectrics are part of a small subgroup of noncentrosymmetric crystals. Related properties are piezoelectricity and pyroelectricity. Dielectrics belonging to all but one of the groups of noncentrosymmetric crystals are piezoelectric. Pyroelectric crystals form another subgroup of 10 types of crystal having especially low symmetry, as shown in Table 31.5.

- All ferroelectrics are pyroelectric and piezoelectric.
- All pyroelectrics are piezoelectric.
- All piezoelectrics are not pyroelectric.
- All pyroelectrics are not ferroelectrics.

31.2 FERROELECTRICITY

Ferroelectrics exhibit an electric dipole moment in the absence of an external electric field. The direction of the dipole moment may be switched by application of an alternating field. This property of polarization reversal and remanence cannot be predicted simply by looking at the structure of a material; it must be determined experimentally.

FERROELECTRICS
Ferroelectrics do not contain iron. The term comes from the analogy with ferromagnetism, which also does not require Fe.

Ferroelectricity is a property that is not only associated with ceramics, certain polymers, such as polyvinylidene fluoride (PVDF), and copolymers between PVDF and trifluoroethylene are ferroelectric. PVDF is a semicrystalline polymer. The crystalline conformation has an orthorhombic unit cell (mm2).

A ferroelectric crystal consists of regions called domains. Within each domain the polarization is in a common direction, but in adjacent domains the polarization is in a different direction, as illustrated in Figure 31.4. The net polarization then depends on the difference in the volumes of the two domain orientations. If the volumes are equal, the material does not exhibit a net polarization. By etching in a suitable chemical, we can see the domain structure. This is analogous to the process we described in Section 12.3 to reveal dislocations.

Domain walls separate adjacent domains and are transition regions where the direction of polarization changes. They have a width on the order of one lattice parameter (~0.2–0.3 nm), but this varies with temperature and crystal purity. This is less than one hundredth as thick as the Bloch walls between magnetic domains in ferromagnets (see Chapter 33). Figure 31.5 illustrates a domain wall in a ferroelectric. There are actually two types.

- 90° wall — polarization vectors in adjacent domains at right angles
- 180° wall — polarization vectors in adjacent domains are antiparallel

The wall energy is of the order of 10 mJ/m^2. You can compare this value to typical grain boundary (GB) energies that are 0.1–0.3 mJ/m^2 for low-angle boundaries, 0.5–0.6 J/m^2 for high-angle tilt boundaries, and 0.8–0.9 J/m^2 for high-angle twist boundaries. As a consequence, it is, in general, easier to move domain boundaries than it is to move GBs.

Ferroelectricity depends on temperature. Above θ_c, ferroelectric behavior is lost, and the material becomes paraelectric. The change from the ferroelectric to the nonferroelectric state is accompanied either by a change in crystal symmetry (e.g., as in $BaTiO_3$) or by an order–disorder transition, such as in the organic ferroelectric compound triglycine sulfate (TGS).

The relative permittivity shows a characteristic peak at T_{cw}, as shown in Figure 31.6, and falls off at higher temperatures following the Curie-Weiss law.

$$\varepsilon_r - 1 = \chi = C/(T - T_{cw}) \tag{31.9}$$

Curie constants and Curie temperatures for several ferroelectric ceramics are given in Table 31.6.

- For ferroelectrics that undergo a first-order transition [e.g., $BaTiO_3$, $(Ba,Sr)TiO_3$, $PbTiO_3$, $KNbO_3$], $T_{cw} < \theta_c$. A first-order transition involves a discontinuous change in P with T.
- For ferroelectrics that undergo a second-order transition (e.g., TGS, Rochelle salt, dihydrogen phosphate), $T_{cw} \sim \theta_c$. The change in P is continuous for a second-order transition.

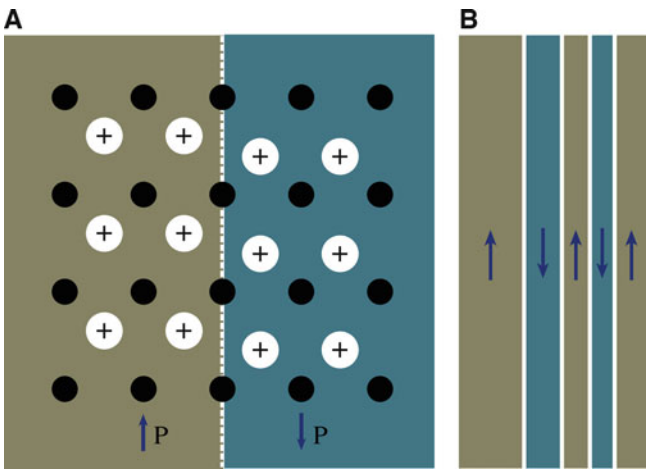


FIGURE 31.4. (A) Ionic displacements in two 180° ferroelectric domains. (B) Domain structure showing several 180° domains of different sizes.

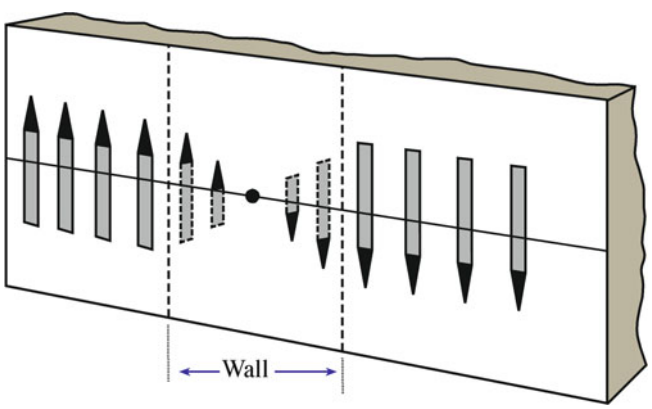


FIGURE 31.5. A 180° domain wall. The width is ~0.2–0.3 nm.

31.3 $BaTiO_3$: THE PROTOTYPICAL FERROELECTRIC

Barium titanate ($BaTiO_3$) was the first ceramic in which ferroelectric behavior was observed and is probably the most extensively investigated of all ferroelectrics. Its discovery made available κs up to two orders of magnitude greater than had been known before. This property was very soon utilized in capacitors, and $BaTiO_3$ remains the basic capacitor dielectric in use today (although not in its pure form). There are several reasons why $BaTiO_3$ has been so widely studied.

- Relatively simple crystal structure
- Durable
- Ferroelectric at room temperature ($\theta_c = 120°C$)
- Easily prepared as a polycrystalline ceramic, single crystal, or thin film

31.3.1 Structure and Structural Transformations

Above θ_c, the unit cell of $BaTiO_3$ is cubic (point group m3m), with the ions arranged as shown in Figure 7.2.

Recap: Each Ba^{2+} is surrounded by 12 nearest-neighbor oxygen ions; each Ti^{4+} has six oxygen ion neighbors. Together, the Ba^{2+} and O^{2-} ions form a face-centered cubic (fcc) arrangement, with Ti^{4+} fitting into the octahedral interstices. The octahedral site is actually expanded because of the large Ba^{2+} ions ($r_{Ba^{2+}} = 0.136$ nm). The Ti^{4+} ion is quite small ($r_{Ti^{4+}} = 0.064$ nm), giving a radius ratio with oxygen ($r_{Ti^{4+}}/r_{O^{2-}}$) of 0.44. This value is close to the limiting value (≥ 0.414) for a coordination number of 6. The result is that the Ti^{4+} often finds itself off-centered within its coordination octahedron. This is why it is sometimes referred to as the "rattling" titanium ion (think back to Pauling's rules). The direction of off-centering may be along one of the 6 <001> directions or along one of the 8 <111> directions or 12 <110> directions.

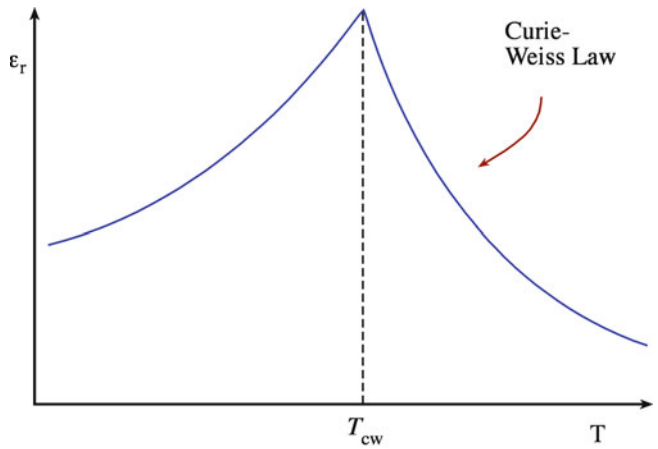


FIGURE 31.6. Relative permittivity of a ferroelectric as a function of temperature.

At temperatures $>\theta_c$, the Ti^{4+} has no fixed unsymmetrical position, and hence there is no permanent dipole moment. The crystal is paraelectric; it can be polarized only while in an applied electric field.

On cooling $BaTiO_3$ below θ_c, the structure spontaneously changes to the tetragonal form (point group 4 mm) with a dipole moment along the *c* axis, as shown in Figure 31.7. The magnitude and direction of the ion displacements accompanying this transformation are given in the figure.

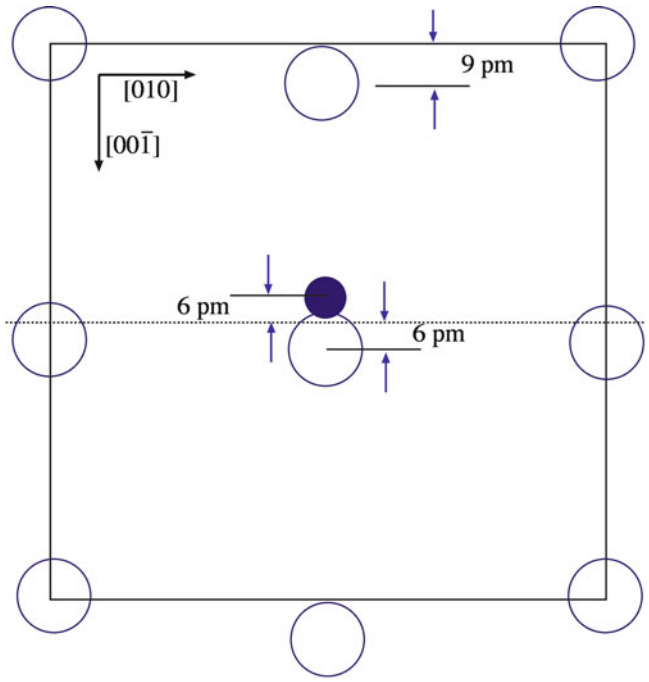


FIGURE 31.7. [100] Projection of $BaTiO_3$ shows ion displacements below θ_c (not to scale).

TABLE 31.6 Curie Temperatures and Curie Constants for Several Ferroelectric Ceramics

Ceramic	*Structure*	θ_c *(K)*	*C* (10^4 *K)*	*Oxide*	*Structure*	θ_c *(K)*	*C* (10^4 *K)*
$SrTiO_3$	Perovskite	~0	7.0	$LiNbO_3$	Ilmenite	1,470	
$BaTiO_3$	Perovskite	373	12.0	$LiTaO_3$	Ilmenite	890	
$PbTiO_3$	Perovskite	763	15.4	$Cd_2Nb_2O_7$	Pyrochlore	185	7.0
$CdTiO_3$	Perovskite	1,223	4.5	$PbNb_2O_6$	Tungsten bronze	843	30.0
$KNbO_3$	Perovskite	712	27.0				

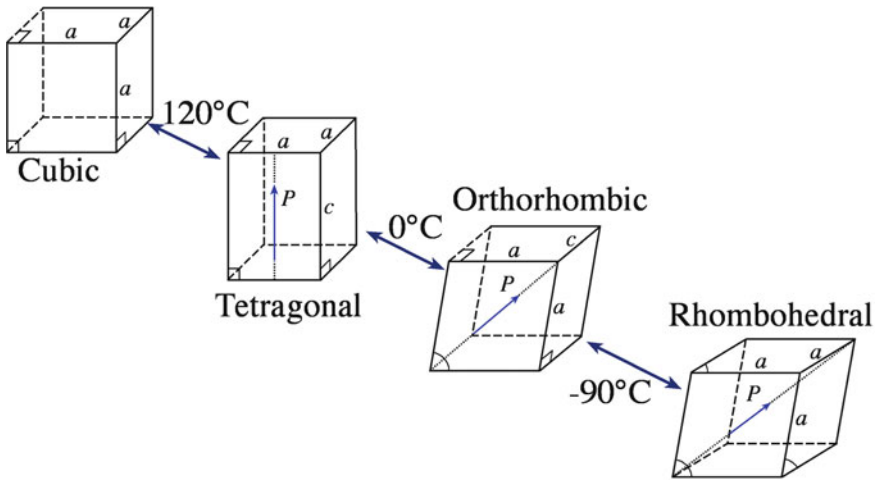


FIGURE 31.8. $BaTiO_3$ polymorphs show the direction of polarization.

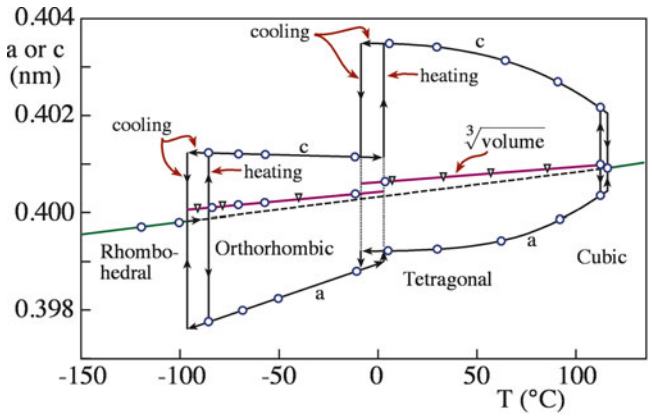


FIGURE 31.9. Experimental measurements of lattice parameters of $BaTiO_3$ as a function of temperature. (Note the change in volume at each transition and the hysteresis in the lattice parameters).

There are other structural transformations that occur in $BaTiO_3$, as shown in Figure 31.8.

- Below 0°C, the unit cell is orthorhombic, with the polar axis parallel to a face diagonal. Application of an electric field along [011] causes the domains to adopt this direction of Ti^{4+} off-centering.
- Below −90°C, the structure is rhombohedral, with the polar axis along a body diagonal. The Ti^{4+} is off-centered along [111].

Because these transformations both occur below room temperature, they are not commercially important.

The phase changes that occur in $BaTiO_3$ are characterized by an expansion of the original cubic lattice in the direction of spontaneous polarization and a contraction in the perpendicular direction. The temperature dependence of the lattice parameters of $BaTiO_3$ in the four phases is shown in Figure 31.9.

CALCULATION OF THE DIPOLE MOMENT FOR $BaTiO_3$

Using equation 33.1 we need to consider the distances that the Ti^{4+} and O^{2-} ions are displaced from their regular (cubic) lattice positions (assuming the position of the Ba^{2+} ions is fixed). The charge is the product of q and the ion charge. The dipole moments are then

$$\mu(Ti^{4+}) : (1.602 \times 10^{-19}C)(4)(0.06 \times 10^{-8}cm)$$
$$= 3.84 \times 10^{-28}C.cm$$

$$\mu(O^{2-}top) : (1.602 \times 10^{-19}C)(2)(0.09 \times 10^{-8}cm)$$
$$= 2.88 \times 10^{-28}C.cm$$

$$\mu(O^{2-}side) : (1.602 \times 10^{-19}C)(2)(0.06 \times 10^{-8}cm)$$
$$= 1.92 \times 10^{-28}C.cm$$

Now we need to include the number of each of the types of ions per cell. There is a single Ti^{4+}/cell, there is on top-face O^{2-}/cell, and two side-face O^{2-}/cell.
The total dipole moment per unit cell is

$$\mu = \mu(Ti^{4+}) + \mu(O^{2-}top) + 2\mu(O^{2-}side)$$
$$= 1.056 \times 10^{-27}C.cm$$

31.3.2 Properties of $BaTiO_3$

Barium titanate is ferroelectric and, by implication, also pyroelectric and piezoelectric. The characteristic of a ferroelectric is that it is polarized in the absence of an applied electric field, and the direction of polarization can be

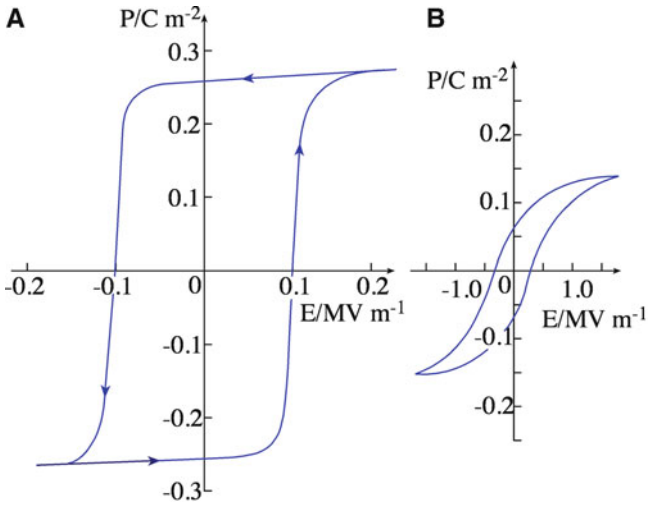


FIGURE 31.10. Hysteresis loops for $BaTiO_3$. (A) Single-domain single crystal. (B) Polycrystalline ceramic.

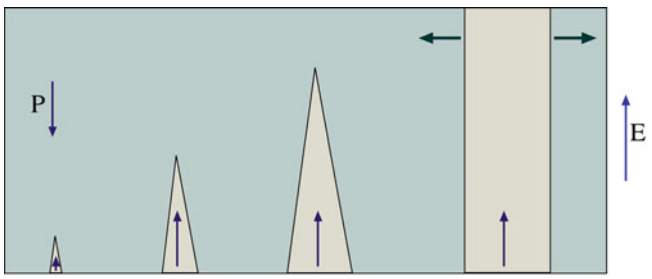


FIGURE 31.11. Growth of a ferroelectric domain in a field, ξ.

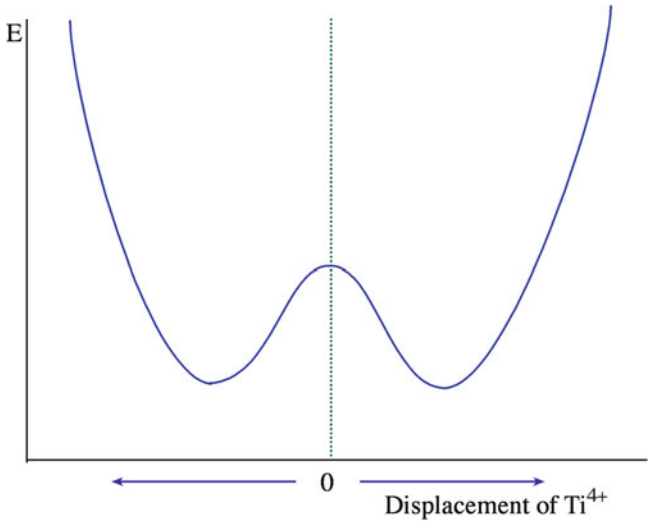


FIGURE 31.12. Potential energy wells for Ti^{4+} as a function of displacement within the octahedral site.

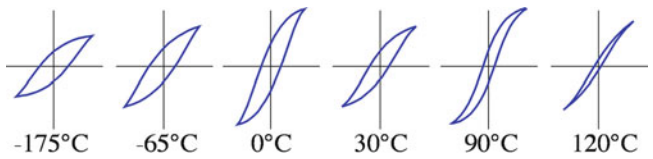


FIGURE 31.13. Hysteresis loops for $BaTiO_3$ as a function of temperature.

reversed. Figure 31.10 shows a rectangular hysteresis loop for a single-domain single crystal of $BaTiO_3$. This loop was obtained at room temperature using a 50-Hz supply. E_c is 0.1 MV/m, and P_s is 0.27 C/m^2.

In tracing out the hysteresis loop, both 180° and 90° changes in domain orientation take place The almost vertical portions of the loop are due to reversal of the spontaneous polarization as antiparallel 180° domains nucleate and grow, as illustrated in Figure 31.11. This process corresponds to the Ti^{4+} moving from one of its off-center sites along the *c* axis to the other site. There is a potential barrier to this movement, as indicated by Figure 31.12.

The motion of domain walls in ferroelectrics is not simple. In an electric field, a 180° wall in $BaTiO_3$ appears to move by the repeated nucleation of steps by thermal fluctuations along the parent wall. Domains misoriented by 180° tend to switch more easily than 90° domain walls because no net physical deformation is required; domains misoriented by 90° are inhibited from changing orientation by the strain that accommodates switching *c*- and *a*-axes.

The almost horizontal portions of the hysteresis loop represent saturated states, in which the crystal is single domain during a cycle. Defects and internal strains within the crystallites impede the movement of domain walls. Domain wall mobility has been found to decrease with time (even without applied mechanical or electrical stress or thermal changes). This is due to internal fields associated with charged defects, redistribution of lattice strains, and accumulation of defects at domain walls.

The hysteresis loop of a polycrystalline $BaTiO_3$ ceramic has a higher E_c and lower P_r than the single crystal.

The size of the hysteresis loop also depends on temperature, as shown in Figure 31.13. At low temperatures, the loops is fatter and E_c is greater, corresponding to a larger energy required to domain reorientation. At higher temperatures, E_c decreases until at θ_c no hysteresis remains and the material becomes paraelectric.

Figure 31.14 shows the temperature dependence of the dielectric constant of single-crystal $BaTiO_3$. The high value of κ appears over a very short temperature range, close to θ_c and far from room temperature. For this reason, pure $BaTiO_3$ is not particularly useful as a dielectric. Ideally, κ must be:

- High at room temperature
- Stable over as wide a temperature range as possible

There are several approaches that can be used to increase lower θ_c and increase κ at room temperature.

- Form a solid solution with an isostructural compound (see Section 31.4)
- Reduce the grain size, as shown in Figure 31.15

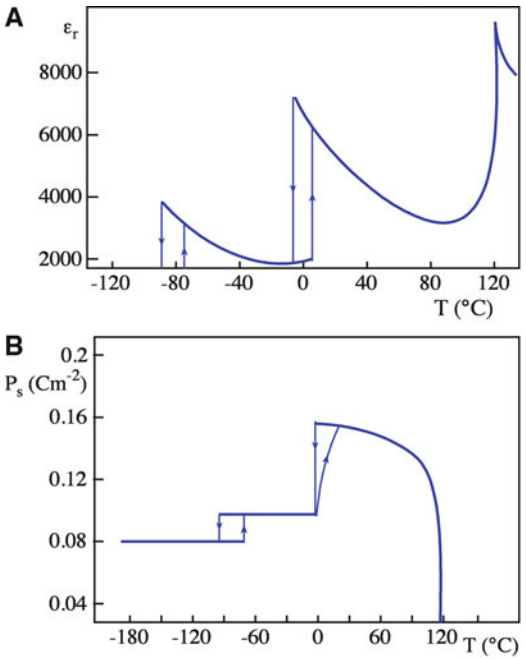


FIGURE 31.14. (A) Dielectric constant and (B) spontaneous polarization of single-crystal $BaTiO_3$ as a function of temperature. (Compare to Figure 31.9).

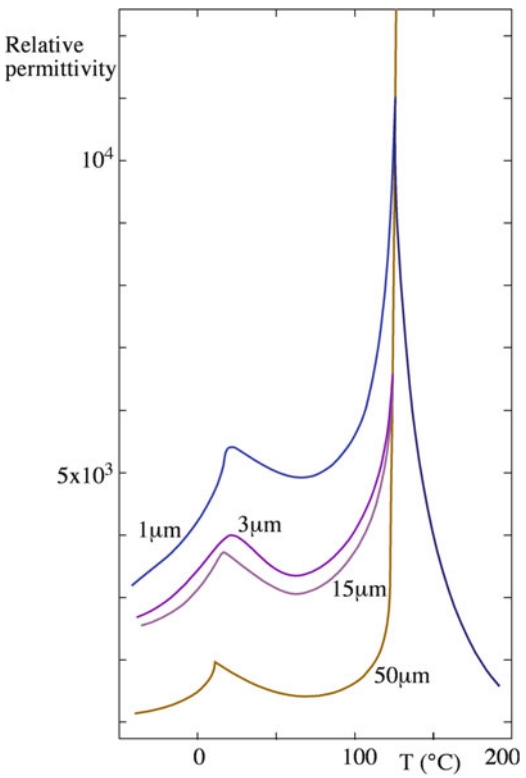


FIGURE 31.15. Effect of grain size on the dielectric constant of $BaTiO_3$.

- Induce mechanical stresses (compressive or tensile) in thin films because of differences in lattice parameter between the film and the substrate (e.g., θ_c for $BaTiO_3$ thin films on MgO and on Pt are lower than for bulk material).

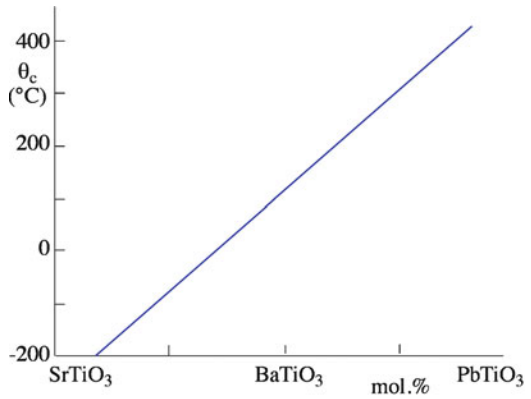


FIGURE 31.16. Effect of substitution on θ_c for $BaTiO_3$ solid solutions with $SrTiO_3$ and $PbTiO_3$.

TABLE 31.7 Some Other Ferroelectric Ceramics

Compound	*θ_c (°C)*
$SrTiO_3$	−245
$PbTiO_3$	490
$KNbO_3$	435
$KTaO_3$	−260
$Cd_2Nb_2O_7$	−85
$PbNb_2O_6$	570
$LiNbO_3$	1,200

31.4 SOLID SOLUTIONS WITH $BaTiO_3$

$BaTiO_3$ is rarely used in its pure form because, as we mentioned in the previous section, the high κ occurs only over a very short temperature range that is far from room temperature. Solid solutions with an isostructural compound can broaden θ_c as well as shift it to lower temperatures. One important solid solution phase is that formed between $BaTiO_3$ and $SrTiO_3$. These solid solutions are often referred to as BST. Solid solutions of $BaTiO_3$ and $PbTiO_3$ lead to an increase in θ_c over that of pure $BaTiO_3$. The effect on substitution of either Sr^{2+} or Pb^{2+} for Ba^{2+} in $BaTiO_3$ is shown in Figure 31.16.

31.5 OTHER FERROELECTRIC CERAMICS

Table 31.7 lists some other ferroelectric ceramics. This table does not include the large number of solid solution phases that are ferroelectric. Many ferroelectric ceramics have the perovskite structure above θ_c, but this is not a prerequisite. For example, $LiNbO_3$ has the ilmentite ($FeTiO_3$) structure, and $Cd_2Nb_2O_7$ has the pyrochlore structure (the mineral pyrochlore is $CaNaNb_2O_6F$).

31.6 RELAXOR DIELECTRICS

$BaTiO_3$ and most related compositions show little change in dielectric properties with frequency until the gigahertz range is reached. Relaxor dielectrics are a class of perovskite ferroelectrics that show significant changes in κ and tan δ with frequency. The classic high-κ relaxor is lead magnesium niobate ($PbMg_{1/3}Nb_{2/3}O_3$, or PMN), which was first synthesized in the late 1950s.

In addition to the high κ of many relaxor compositions, they also have a broad peak in permittivity versus temperature, even in the absence of additives and even in the form of single crystals. This behavior is attributed to nanoscale (~10 nm)-ordered regions, which are too small to yield the sharp phase transition of normal ferroelectrics. As a result, spontaneous polarization and associated ferroelectric properties are retained over a very broad temperature range. Another attractive feature of relaxors is that dense polycrystalline ceramics are achievable at relatively low sintering temperatures (≤900°C), which allows a significant reduction in the amount of Pd used in Ag-Pd metallizations for electrodes in multilayer capacitors (see Section 31.7).

NOTATION FOR *C*

We use *C* for capacitance and *C* for Curie constant. There is really no way around this potential confusion; fortunately both terms rarely occur in the same equation.

One of the difficulties with most relaxor compositions containing Pb and Nb is that they have a tendency to form the lower κ pyrochlore-type rather than perovskite structures. The pyrochlore-type phase found in PMN has the composition $Pb_{1.83}Nb_{1.71}\ Mg_{0.29}O_{6.39}$. It has a room temperature κ of 130 and is paraelectric.

There are a whole range of lead-containing relaxors based on lead zinc niobate (PZN), lead iron niobate (PFN), lead iron tungstate (PFW), and solid solutions with each other and with $BaTiO_3$ (BT), $PbTiO_3$ (PT), and $SrTiO_3$ (ST). Some of the solid-solution phases are PMN-PT, PMN-PT-PZN, PMN-PZN, PFN-PFW, PFN-PMN, and PFW-PT.

31.7 CERAMIC CAPACITORS

Capacitance is defined as the total charge stored by the capacitor divided by the applied potential.

$$C = Q/V \tag{31.10}$$

It depends on the:

- Dielectric between the conductors
- Area of each conductor, *A*
- Separation between them, *d*

For a parallel plate capacitor in a vacuum

$$C = \varepsilon_0 A/d \tag{31.11}$$

When a dielectric is present, polarization occurs and permits additional charge to be stored. The ability of the dipoles in the dielectric to polarize and store charge is reflected by ε:

$$C = \varepsilon A/d \tag{31.12}$$

or in terms of κ:

$$C = \kappa\varepsilon_0 A/d \tag{31.13}$$

There are three main types of capacitor.

- Ceramic
- Paper or polymer film
- Electrolytic (aluminum or tantalum)

Frequency ranges where these capacitor types are usable and the capacitance values of each type are shown in Table 31.8. Ceramic capacitors occupy about 30% of the total capacitor market, with sales of over 80 billion discrete units per year.

We can distinguish three basic types of ceramic capacitor.

- Film capacitors used in memory devices
- Single-layer discrete capacitors, usually disk capacitors
- Multilayer chip capacitors (MLCCs)

Each of these types is described separately. Film capacitors that are used in memory devices are integrated with the other circuit components. On the other hand, disk capacitors and MLCCs are discrete components.

31.7.1 Categories of Ceramic Capacitor Dielectric

Ceramic capacitors are generally classified into three types based on their properties.

TABLE 31.8 Frequency and Capacitance Ranges for Capacitor Types

Capacitor	*Maximum useable frequency (Hz)*	*Range of capacitance values (μF)*
Mica	10 G	$0.1–10^{-6}$
Paper/polymer	10 G	$100–10^{-6}$
Ceramic	10 G	$10^{3}–10^{-6}$
Al electrolytic	10 k	$10^{6}–0.1$
Ta electrolytic	10 k	$10^{3}–0.1$

Class 1 or *NPO* These have $\kappa < 15$ and are mainly used for electrical insulation, such as substrates, power line insulators, and spark plug insulators. Medium κ class 1 capacitors are used in:

- High-power transmitter capacitors in the frequency range 0.5–50 MHz because of their low tan δ
- Stable capacitors for general electronic use in the frequency range 1 kHz to 100 MHz because of the stability of capacitance with temperature
- Microwave resonant cavities operating at 0.5–50 GHz because of their stability and low tan δ

Class 2 These are high dielectric constant ceramics based on $BaTiO_3$. The two main subclasses are Z5U and X7R after the scheme shown in Table 33.5 that was devised by the Electronics Industries Association (EIA) in the United States for specifying the variability of capacitance with temperature in the range of practical interest (Table 31.9). For maximum capacitance, θ_c is shifted close to room temperature and broadened. Shifters form solid solution phases with $BaTiO_3$. Depressor additives result in broadening of the peak and then concentrate at the grain boundaries (GBs). Compositions and properties of some Z5U and X7R dielectrics are shown in Tables 31.10 and 31.11, respectively.

Class 3 These are based on either $BaTiO_3$ or $SrTiO_3$ (usually X7R type) and have very high "apparent" dielectric constants ($\kappa = 50{,}000$–$100{,}000$), which are achieved by producing either a surface layer on the grains or at the GBs that is electrically insulating whereas the grains themselves are conducting or semiconducting. This can be achieved in two ways.

- The ceramic is first heated to high temperature (900–1,000°C) under reducing conditions (usually a H_2/N_2 mixture) that makes it semiconducting, and then the surface layer is reoxidized by heating in oxygen at a lower temperature.

TABLE 31.9 EIA Coding of Class 2 Capacitors

Code	*Temperature range (°C)*	*Code*	*Capacitance change (%)*
X7	−55 to +125	D	±3.3
X5	−55 to +85	E	±4.7
Y5	−30 to +85	F	±7.5
Z5	+10 to +85	P	±10
		R	±15
		S	±22
		T	+22 to −33
		U	+22 to −56
		V	+22 to −82

TABLE 31.10 Composition and Properties of Z5U Dielectrics

	Composition (wt%)			
Component	*1*	*2*	*3*	*Role*
$BaTiO_3$	84–90	65–80	72–76	Base material
$CaZrO_3$	8–13	—	—	Shifter
$MgZrO_3$	0–3	—	—	Depressor
$SrTiO_3$	—	7–11	5–8	Shifter
$CaTiO_3$	—	7–11	4–6	Depressor
$BaZrO_3$	—	7–11	7–10	Shifter
$CaSnO_3$	—	—	2–4	Shifter
Other oxides (e.g., Nb_2O_5)	1–3	8–13	0–3	Acceptors
κ (25°C, 1 kHz)	5,700–7,000	5,500–6,500	11,500–13,000	
Tan δ	$\leq$0.03	$\leq$0.03	$\leq$0.03	

TABLE 31.11 Composition and Properties of X7R Dielectrics

	Composition (wt%)			
Component	*1*	*2*	*3*	*Role*
$BaTiO_3$	90–97	85–92	86–94	Base material
$CaZrO_3$	2–5	4–8	—	Shifter
$BaCO_3$	0–5	—	—	Stoichiometry adjuster
$SrTiO_3$	—	3–6	—	Shifter
Bi_2O_3			5–10	Depressor, flux
Other	2–5	1–4	2–6	
κ (25°C, 1 kHz)	1,600–2,000	1,800	1,400–1,500	
Tan δ	$<$0.025	$<$0.025	$<$0.015	

- The GBs can be made insulating by diffusing a low-melting-point mixture of metal oxides, such as CuO, MnO, and Bi_2O_3. The very thin (<10 nm) insulating layers and the high GB area produces very high capacitances.

The properties of these dielectrics are similar to those in class 2, but their working voltages are 2–25 V. The big advantage is that simple disk capacitors can be produced with large capacitances, >1 μF.

31.7.2 Disk Capacitors

Figure 31.17 shows an example of a ceramic disk capacitor. Disc diameters range from 2 to 30 mm, and dielectric thicknesses are 50 μm to 2 mm.

These capacitors are common but from a practical standpoint can store only a limited amount of charge. To increase the storage capacity, it would be necessary to increase the overall size or decrease the distance between the plates. The first option would make the component too bulky. The second option would increase the possibility of dielectric breakdown.

MLCC ADVANTAGES

Small
Inexpensive
Good frequency response
Can be surface mount
High capacitance
Easy to make

The first disk capacitors used mica sheets. Mica has very high dielectric strength (see Table 31.4) and can readily be cleaved into thin sheets. Nowadays, disk capacitors are made from $BaTiO_3$-based compositions using traditional ceramic processing methods. The powder is mixed with 5–10 vol.% of an organic binder and pressed into a disk. Alternatively, they can be punched from extruded ribbon or tape. The green ceramic is then sintered at 900–1,300°C in air to produce a dense material. After sintering, Ag paint is applied to the major surfaces, and the disks are briefly refired at 600–800°C. Tinned copper wires are soldered to the metallized ceramic disk before the whole assembly is immersed in a polymer (usually an epoxy resin).

Disk capacitors are made using all classes of capacitor dielectric, allowing a wide range of capacitances.

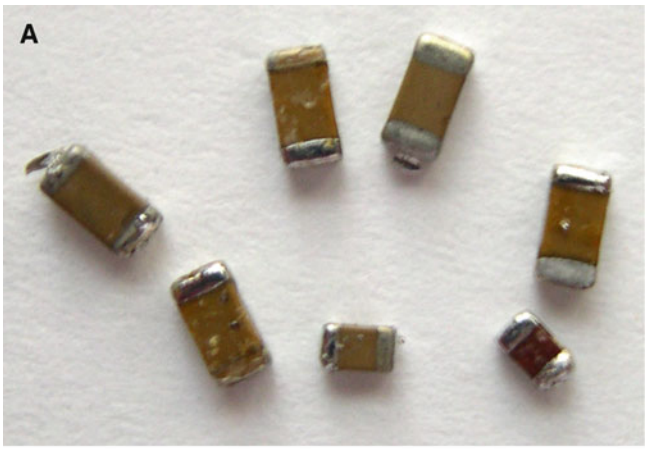
0.1–1,000 pF using class I dielectrics
1,000–100,000 pF using class II dielectrics
0.1–2.0 μF using class III dielectrics

FIGURE 31.17. Ceramic disc capacitor.

31.7.3 Multilayer Chip Capacitors

The largest class of ceramic capacitors produced, in number and in value, is the MLCC. More than 80 billion "chips" are manufactured worldwide each year.

Figure 31.18 shows several MLCCs and their structures. The external dimensions range from



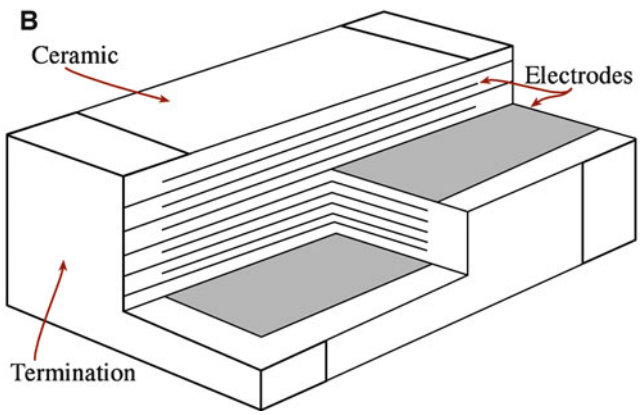


FIGURE 31.18. (A) Ceramic multilayer chip capacitor. (B) Electrode structure.

1.25 × 1.0 × 1.0 mm thick up to 6.0 × 6.0 × 2.25 mm thick. The interelectrode spacing is typically about 20 μm. Capacitance values have been produced from 1 pF up to 300 μF. Class 1 and class 2 dielectrics are mainly used for MLCCs. Increased performance has been obtained using relaxor dielectrics, such as lead iron niobate (PFN) and lead magnesium niobate (PMN).

31.7.4 Fabricating MLCCs

There are several different ways to make MLCCs. The basic steps are:

- Preparing the slurry. The slurry may contain up to 35 vol.% of liquid. Water-based slurries containing a latex binder are often used, although for some powder formulations an organic based slurry is required.
- Tape casting.
- Drying.
- Cutting of dried sheets into typically 15-cm squares.
- Screen printing Ag-Pd electrodes. The cost of the electrode materials is a big concern. In fact, the noble metals account for more than half the cost price of MLCCs. Alternative nonprecious metals such as copper and nickel have been used. A different approach to reducing cost of metallization is the "fugitive" electrode process. The electrodes are made of carbon, which is removed during sintering in air. The remaining cavities are then pressure-infiltrated with either molten lead or a tin-lead alloy to produce the electrodes.
- Stacking the electroded sheets.
- Laminating.
- Dicing.
- Burning out the binder. This step of the process must be very carefully controlled. There is a lot of binder to be removed, and if burnout is too rapid the sheets may delaminate.
- Sintering. Typical sintering temperatures are 1,200–1,400°C in air. If nonprecious metals are used, the furnace atmosphere must be very carefully controlled to avoid oxidation. Atmospheres of N_2 and $H_2 + N_2$ have been used.
- Application of external electrodes. The ends of the chips can be dipped into an Ag-Pd ink. Pure Ag can be used (which is cheaper), but it must be coated with Ni to increase solder leach resistance and then by Sn to maintain solderability.

31.8 CERAMIC FERROELECTRICS FOR MEMORY APPLICATIONS

An important potential application for ferroelectrics is their incorporation as thin films into dynamic random access memories (DRAMs). The majority of the memory in a computer is DRAM. Information is stored in millions of tiny capacitors, each representing a single bit. The capacitors used in DRAM chips are fabricated directly onto the silicon substrate.

The dielectrics currently used in DRAMs are:

- SiO_2, which can be produced by thermal oxidation of Si
- A combination of SiO_2 and Si_3N_4, (which is often referred to as "ONO" because the dielectric consists of alternating layers of SiO_2 and Si_3N_4)

The bottom electrode is the doped (often n-type) silicon substrate; the top electrode is either polysilicon or aluminum. The limitation of both SiO_2 and Si_3N_4 is that they have low κ.

The dielectric constant of SiO_2 is 3.9. A 100 nm thick SiO_2 film yields a capacitance of 3.4×10^{-16} F/μm^2 (31 fF/μm^2).

The dielectric constant of Si_3N_4 is 6. A 100-nm Si_3N_4 film yields a capacitance of 53 fF/μm^2.

To push memory densities beyond 64 Mbits using SiO_2 or ONO dielectrics, it has been necessary to develop very complicated three-dimensional structures such as trench capacitors.

Being able to use a dielectric with a large κ would allow a decrease in the required surface area, avoid stacking and trenching, and allow planar configurations. Such configurations are easier and cheaper to fabricate and provide high production yields.

Thin films of BST have been the most widely studied dielectric for ferroelectric DRAMS. The highest capacitance reported for a BST dielectric is 145 fF/μm^2, which was achieved with a 20-nm film of a material having $\kappa = 325$. Prototype BST capacitor DRAMS were first reported in 1995 but have not been widely used commercially because of the advances in other storage technologies.

31.9 PIEZOELECTRICITY

Piezoelectricity—pronounced P (the letter) A (the letter) zow (like toe)—is a reversible property possessed by a select group of materials that don't have a center of symmetry. When a dimensional change is imposed on the dielectric, polarization occurs and a voltage or field is created. This is the direct effect. When an electric field is applied to a dielectric, polarization may change its dimensions. This is the inverse effect, also called electrostriction. Dielectric materials that display this reversible behavior are piezoelectric.

The ξ produced by the stress T is:

$$\xi = gT \tag{31.14}$$

The strain, S, produced by ξ is:

$$S = d\xi \tag{31.15}$$

where d and g are piezoelectric coefficients related through Young's, $\mathcal{E}$.

$$\mathcal{E} = 1/gd \tag{31.16}$$

- High d coefficients are desirable for dielectrics that are utilized in motional or vibrational devices, such as sonor and transducers in ultrasonic cleaners.
- High g coefficients are desirable for dielectrics used to produce voltages in response to mechanical stress, such as in gas igniters.

The equations of state that describe a piezoelectric crystal in regard to its electric and elastic properties are, in their general form:

$$\text{Direct effect} \quad D = dT + \varepsilon^T \xi \tag{31.17}$$

$$\text{Inverse effect} \quad S = s^{\xi} T + d\xi \tag{31.18}$$

The only new variable here is s, the material compliance (inverse of stiffness). The superscripts in equations 31.17 and 31.18 denote the parameters that are held constant. For example, s^{ξ} is the compliance at constant ξ.

STRESS AND STRAIN

We use S for the strain and T for the stress (not ε and σ, which are more typical) to avoid possible confusion with permittivity that is almost always represented by ε

When written in matrix form, these equations relate the properties to the crystallographic directions. For ceramics and other crystals, the piezoelectric constants are anisotropic. For this reason, they are expressed in tensor form. The directional properties are defined by the use of subscripts. For example, d_{31} is the piezoelectric strain coefficient where the stress or strain direction is along the 1 axis and the dielectric displacement or electric field direction is along the 3 axis (i.e., the electrodes are perpendicular to the 3 axis). The notation can be understood by looking at Figure 31.19.

Another important parameter of a piezoelectric is the electromechanical coupling coefficient, k, which is a measure of the ability of the material to convert electrical energy to mechanical energy or vice versa.

For the direct effect:

$$k^2 = \frac{\text{mechanical energy converted to electrical energy}}{\text{input mechanical energy}} \tag{31.19}$$

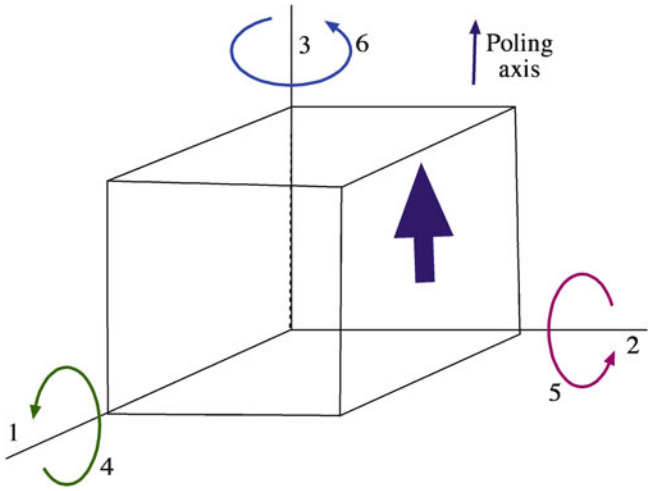


FIGURE 31.19. Notation of axes for piezoelectric ceramic.

For the indirect effect:

$$k^2 = \frac{\text{electrical energy converted to mechanical energy}}{\text{input electrical energy}} \tag{31.20}$$

Because the conversion of electrical energy to mechanical energy (or vice versa) is always incomplete, k^2 is always <1, and so k is also <1. Values of k in piezoelectric ceramics range from 0.1 to 0.9, as shown in Table 31.12. Rochelle salt is the classic example of a piezoelectric because k is so large.

TABLE 31.12 Properties of Some Piezoelectric Ceramics

Material	*Piezoelectric coefficient (10^{-12} C/N)*	*Electromechanical coupling factor (k)*
Quartz (X cut)	$d_{21} = 2.25$	
	$d_{33} = 2.3$	0.10
$BaTiO_3$	$d_{31} = -75$	0.48
PZT	$d_{33} = 374$	0.67
Lead metaniobate	$d_{33} = 85$	0.42
Lithium niobate	$d_{33} = -1$	
	$d_{15} = 68$	0.40
Rochelle salt (45° X cut)	$d_{14} = 870$	0.78

31.10 LEAD ZIRCONATE-LEAD TITANATE SOLID SOLUTIONS

Solid solutions between lead zirconate ($PbZrO_3$) and lead titanate ($PbTiO_3$) are known by the acronym PZT and are the most widely used of all piezoelectric ceramics.

Lead zirconate is orthorhombic at room temperature: a = 0.588 nm, b = 1.176 nm, and c = 0.820 nm. It is antiferroelectric, with $\theta_c = 231°C$. The dipoles due to the displacement of the Zr^{4+} ion from the center of the octahedral site are in opposite directions in adjacent unit cells so that the net P is zero.

Lead titanate is isomorphous with $BaTiO_3$, with a = 0.390 nm and c = 0.415 nm. It is ferroelectric at room temperature with a $\theta_c = 495°C$ (the highest known value among perovskite ferroelectrics).

The PZT phase diagram is shown in Figure 31.20. The significant feature of this phase diagram is the morphotropic phase boundary (MPB) at a composition where the PZ:PT ratio is almost 1:1. At an MPB, there is an abrupt change in the structure with the composition at a constant temperature. PZT compositions near the MPB have both high k and high κ, as shown in Figure 31.21. This is where commercial PZT compositions are chosen.

The PZT ceramics often contain dopants (in the range 0.05–5.0 at.%) to modify the properties of the material for specific applications.

Examples

Donors (e.g., replacing Zr^{4+} with Nb^{5+} or replacing Pb^{2+} with La^{3+}). To maintain electroneutrality, the addition of these dopants is usually compensated for by the formation of Pb^{2+} vacancies. Donors enhance domain reorientation, and materials produced with these additives are characterized by rectangular hysteresis loops, low E_c, high P_r, high κ, maximum k, high tan δ, high elastic compliance, and reduced aging. Typical applications are in areas where high sensitivity is required, such as hydrophones, sounders, and loudspeakers.

Acceptors (e.g., replacing Zr^{4+} with Fe^{3+}, with the concomitant formation of oxygen vacancies). Domain reorientation is limited, and hence acceptor additives lead to poorly developed hysteresis loops, lower κ, low tan δ, low compliance, and high aging rates. Typical applications are in high-power devices, such as sonar and ultrasonic transducers.

Isovalent (e.g., replacing Pb^{2+} with Ba^{2+} or Sr^{2+} or replacing Zr^{4+} with Sn^{4+}). The substituting ion is of the same valence and approximately the same size as the replaced ion. Solid-solution ranges with these additives are usually quite high and may result in lower θ_c. Hysteresis loops may be poorly developed without additional additives. Other properties include lower tan δ, low compliance, and higher aging rates. These ceramics are used in high-drive applications such as torpedo guidance.

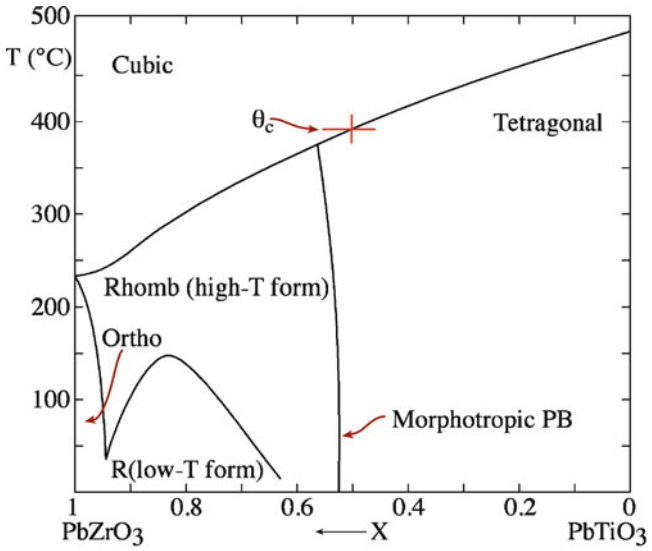


FIGURE 31.20. Lead zirconate titanate (PZT) phase diagram.

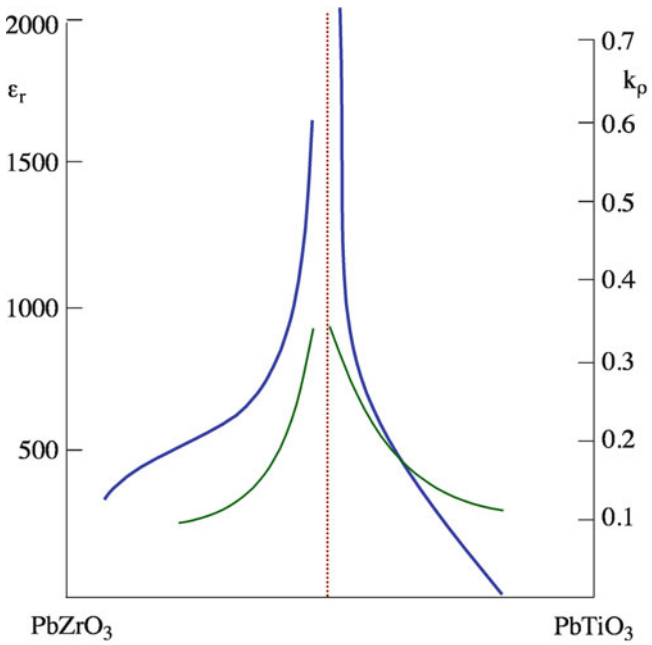


FIGURE 31.21. Dielectric constants and coupling coefficients for PZT compositions near the morphotropic boundary.

The PZT ceramics can be made by normal powder-processing methods. The main difficulty is the high volatility of PbO. To retain as much PbO as possible, sintering may be performed, with the component surrounded by a lead-rich powder such as PZ and enclosed in a lidded crucible. Even with these precautions, there is usually some (typically 2–3%) loss of PbO, which is compensated for by adding additional PbO to the starting batch. A note about safety: lead is toxic, and exposure to lead compounds has a cumulative effect. It is therefore necessary that evaporation is controlled.

31.11 APPLICATIONS FOR PIEZOELECTRIC CERAMICS

Applications for piezoelectric ceramics utilize one of the two piezoelectric effects.

Direct effect – Voltage is produced by means of compressive stress.
Inverse effect – An applied ξ produces small movements. In an alternating field, the piezoelectric vibrates.

31.11.1 Direct Effect

The first commercial piezoelectric $BaTiO_3$ devices were phonograph pickups marketed by Sonotome Corporation in the mid-1940s. They used a so-called bimorph design, where an electrode layer separated two strips of the piezoelectric material. Bimorphs are no longer used for this application because they don't produce high enough quality sound reproduction, and most people use CDs now.

The direct effect is used in high-voltage spark generation for some gasoline engine ignition systems and manually operated gas lighters. In the latter example, which are widely used to ignite natural gas water heaters and other gas-fired domestic appliances, lever-amplified hand pressure generates the voltage. Two electroded piezoelectric cylinders are placed back to back, and a force applied to the cylinders generates a spark across the electrodes. It is important that the force is applied quickly; otherwise, the voltage generated disappears as the charge leaks away. Typical spark energies are ~3 mJ.

MEDICAL ULTRASOUND IMAGING FREQUENCY RANGES

Abdominal, obstetrical, and cardiological applications:

2–5 MHz

Pediatric and peripheral vascular applications:

5–7.5 MHz

Small objects (e.g., the eye), intracardiac and intravascular applications:

10–30 MHz

As in other forms of microscopy, a higher frequency (lower λ) gives better resolution;

~50 μm at 30 MHz

31.11.2 Indirect Effect

Actuators are an important and growing market for piezoelectric ceramics. In applications requiring precise mechanical control, there is a need for a variety of types of actuator. Examples include the positioning of circuit components during the fabrication of integrated and positioning of lenses and mirrors in precise optical equipment. They are also used as positioners for atomic force microscopes and scanning tunneling microscopes.

The natural resonance frequency of a piezoelectric crystal may be used as a frequency standard. Quartz is the material of choice. Quartz crystal resonators provide highly stable crystal-controlled clocks and watches

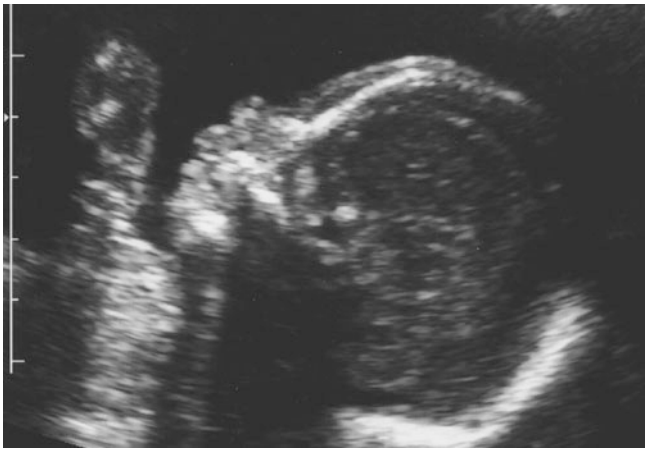


FIGURE 31.22. Medical ultrasound image using ceramic piezoelectric transducers (scale is in centimeters).

(constant to 1 part in 10^9) and control fixed frequencies in communications equipment. Other resonant uses include selective wave filters and transducers for sound generation, as in sonar. PZT ceramics also dominate the market for resonators for ultrasonic cleaners and drilling devices.

Piezoelectric transducers are key components in medical ultrasound imaging and are used both as the acoustic source and the detector (pulse-echo technique). The uses for ultrasound are numerous and include examination of a fetus in the mother's womb, as shown in Figure 31.22, and, at high resolution imaging, intravascular structures. PZT is the ceramic of choice for this application mainly because it has a high κ and is inexpensive compared to some of the other options, such as polymer piezoelectrics.

31.12 PIEZOELECTRIC MATERIALS FOR MEMS

Micro-electro-mechanical systems are devices capable of sensing and responding to a mechanical or an electrical stimulus. One common MEMS device that is in commercial production is the miniature accelerometer (a device used to measure acceleration), which is used to control deployment of an automobile airbag. Ferroelectric and piezoelectric ceramics are materials that fit well into the field of MEMS because of their combined and related electrical/mechanical properties. It is not a necessary requirement that the ceramic

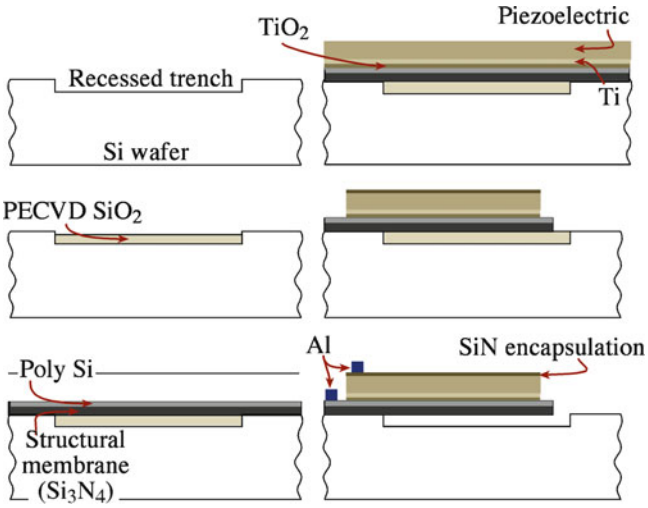


FIGURE 31.23. Steps in the production of a micro-electro-mechanical system cantilever. (A) Create trench by etching. (B) Deposit SiO_2 layer by plasma-enhanced chemical vapor deposition. (C) Deposit Si_3N_4 followed by polysilicon. (D) Deposit the piezoelectric film on an electrode/diffusion barrier system. (E) Pattern and etch. (F) Apply metal contacts and sacrificial etch.

is both ferroelectric and piezoelectric, but if it is ferroelectric the polycrystalline material can be used because it can be poled before use. In nonferroelectric piezoelectric materials such as ZnO, it is necessary to use single crystals with a single domain orientation.

MEMS APPLICATIONS USING PIEZOELECTRIC THIN FILMS

Accelerometers
Acoustic sensors
Infrared detectors
Hot-wire anemometers
Microvalves
Micropumps
Stepper motors

The most widely studied ceramics for MEMS applications are the PZTs because of their high κ and high k. Thin films of PZT have been used in the fabrication of a range of different MEMS and can be integrated with silicon IC processing methods. Figure 31.23 illustrates some of the process steps used to fabricate a cantilever beam microsensor, such as an accelerometer. The actual processing sequence requires over 50 individual steps.

The PZT films can be prepared using physical vapor deposition (PVD) methods such as sputtering, chemical vapor deposition (CVD), and solution processing. Vapor deposition provides uniform films with good step coverage and use methods that are standard in microfabrication facilities. However, there is often a problem with obtaining films of the correct stoichiometry because of the high vapor pressure of PbO. Solution techniques such as sol–gel processing are simple, inexpensive, and give good stoichiometry control, but they result in poor step coverage.

31.13 PYROELECTRICITY

Pyroelectric materials exhibit spontaneous polarization that is a strong function of temperature because the dipole moments vary as the crystal expands or contracts. It was observed in the mineral tourmaline in the seventeenth century. Pyroelectricity occurs in organic crystals such as triglycine sulfate (TGS), ceramics such as $LiTaO_3$, and polymers such as PVDF.

PYROELECTRICS

$LiTaO_3$ (single crystal)	$p = 230\ \mu Cm^{-2}K^{-1}$
$(Sr,Ba)Nb_2O_6$ (single crystal)	$p = 550\ \mu Cm^{-2}K^{-1}$
PZT (polycrystalline)	$p = 380\ \mu Cm^{-2}K^{-1}$

The electric field that develops across a pyroelectric crystal can be extremely large when it is subjected to a small change in temperature, T. A pyroelectric coefficient, p, can be defined as the change in D due to a change in T.

$$p = \frac{\partial D}{\partial T} \qquad (31.21)$$

For example, a crystal with a typical pyroelectric coefficient of 10^{-4} C m^{-2} K^{-1} and $\kappa = 50$ develops a field of 2,000 V/cm for a 1 K temperature change.

31.14 APPLICATIONS FOR PYROELECTRIC CERAMICS

Pyroelectric ceramics can be used to detect any radiation that produces a change in the temperature of the crystal but are generally used for IR detection. Because of their extreme sensitivity, a temperature rise of less than one-thousandth of a degree can be detected. This property finds application in devices such as intruder alarms, thermal imaging, and geographical mapping.

CHAPTER SUMMARY

The uses of dielectrics range from capacitors for storing charge to ultrasound imaging for medical applications. We separate "dielectrics" from "insulators," which we described in the previous chapter, because dielectrics have permanent electric dipoles. If the resultant polarization is spontaneous, we have ferroelectrics. This field is essentially exclusively ceramics. Although some polymers are ferroelectric, they do not find as wide use as ceramics. Also, metals can't be ferroelectric because the charge is not localized.

The requirement of a permanent dipole moment limits useful dielectrics to a select few crystal structures. Therefore, the topic of crystallography is once again important, but we can't predict ferroelectricity by considering crystal structure alone. The most important of the ferroelectric crystals are perovskites. By now you should be gaining an appreciation for the significance of this crystal structure, and we still have some important magnetic perovskites to describe in Chapter 33.

PEOPLE AND HISTORY

Hankel, Wilhelm Gottlieb (1814–1899) (father of Herman Hankel) proposed the word piezoelectricity in 1881. He taught for 10 years in Halle and then moved to Leipzig in 1849 where he was Professor for 40 years. His thesis was titled "De thermoelectricitate crystallorum". Pierre and Jacques Curie had discovered piezoelectricity in 1880.

Seignette, Pierre (1660–1719) He was a French pharmacist who first prepared Rochelle salt in c.1675. In the early literature, the phenomenon of ferroelectricity was more often referred to as "Seignette-electricity" or "Rochelle-electricity."

Valasek, Joseph (1897–1993) discovered ferroelectricity in the 1920s during an investigation of the anomalous dielectric properties of Rochelle salt, $NaKC_4H_4O_6{\cdot}4H_2O$. Rochelle salt is named after the town of La Rochelle (France), where it was first prepared. Valasek was on the faculty at the University of Minnesota from 1919 until he retired in 1965.

Von Hippel, Arthur Robert (1898–2003) reported the ferroelectric properties of $BaTiO_3$ in 1946. Since then, over a hundred pure materials and many more mixed crystal systems that are ferroelectric have been found. He was on the faculty of MIT from 1936 until he retired in 1964. His starting salary was only $3,500 per year, and he is reported to have sold textbooks to pay for medical bills for his children. The Materials Research Society has named one of its major awards in recognition of von Hippel's contribution to "dielectrics, semiconductors, ferromagnetics, and ferroelectrics."

EXERCISES

31.1 What technique would you use to obtain the data shown in Figure 31.9?

31.2 Explain why the hysteresis loops of single crystal and polycrystalline $BaTiO_3$ shown in Figure 31.10 have different E_c and P_s. Would you expect this behavior?

31.3 What would be the appropriate Electronics Industries Association (EIA) code for a capacitor that is required to have a capacitance at room temperature that changes by no more than $\pm 4.7\%$ in the temperature range $-55°C$ to $+125°C$?

31.4 (a) The dielectric strength of lead glass has been measured at two temperatures, 25°C and 200°C. The values obtained are 0.25 MV/cm and 0.05 MV/cm, respectively. Explain why these values are different. (b) A similar study was performed using a 100 nm thick Al_2O_3 film that had been obtained by anodizing Al. The dielectric breakdown was measured to be 16 MV/cm. Why is this value so much higher than that for the polycrystalline Al_2O_3 ceramics listed in Table 31.4?

31.5 Describe how you would expect the polarization of the following ceramics to vary as a function of frequency. Start at 1 MHz and go up to visible light frequencies. (a) Diamond. (b) Al_2O_3. (c) $BaTiO_3$. (d) MgO. (e) AlN.

31.6 Explain the trend in the hysteresis loops shown in Figure 31.13. Sketch the situation at 150°C.

31.7 A parallel plate capacitor is required to store a charge of 50 C at a potential of 5 kV. The separation between the electrodes is 500 m. Determine the plate area if the following dielectrics are used. (a) mica. (b) MgO. (c) $BaTiO_3$. (d) Al_2O_3.

31.8 Estimate the polarization of diamond. Diamond has a diamond-cubic structure with $a = 0.357$ nm.

31.9 Estimate the polarization of MgO. MgO has a rock salt structure with $a = 0.421$ nm.

31.10 Write out, using the Kröger–Vink notation, the effect of the donor and acceptor additions described in Section 31.10.

31.11 Summarize in your own words the four types of polarization encountered in ceramics.

31.12 Memorize the dielectric constants of diamond, NaCl, $BaTiO_3$, Pyrex, and TiO_2. Give a reason for why you want to remember each of them.

31.13 Explain using the concept of a parallel plate capacitor why we want a high dielectric constant to store charge.

31.14 Explain what you mean by the dielectric strength of quartz. Why does high-voltage porcelain have a low dielectric strength?

31.15 When would you want a high dielectric loss and when would you want it to be low?

31.16 What is a ferroelectric, and why are these materials so important today? Give five devices that use them.

31.17 Barium titanate is the prototypical ferroelectric. It is not the best ferroelectric, but it is widely used today. Why? Calculate the dipole moment in barium titanate, showing all the equations you use and any assumptions you make.

31.18 Why is lithium niobate such an interesting material, and when might you use it? Does it have any drawbacks?

31.19 Calculate the capacitance of a 100 nm thick SiO_2 capacitor.

31.20 Summarize the pros and cons of PZT. List its uses and why we are urgently seeking replacements for it.

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J. Materials Science: *Materials in Electronics*

The Materials Research Society (MRS) has offered a number of symposia under the title *Ferroelectric Thin Films*