31

Locally Redistributing Charge

CHAPTER PREVIEW

In this chapter we describe ceramic dielectrics. A dielectric is by definition an electrical insulator (ρ is high and 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. Some of this material may have been covered before but perhaps not specifically in terms 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. Among other things, polarization allows the material to store large amounts of charge: this is a prerequisite for a capacitor. Without dielectrics, computers cannot function; some of today's greatest challenges for the electronics industry concern dielectrics more than semiconductors.

The following key topics are discussed in this chapter:

- 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 microelectromechanical systems (MEMS), sonar, and medical ultrasound imaging.
- The spontaneous polarization of a dielectric depends strongly on T; this is the pyroelectric effect that we use for infrared (IR) detection (e.g., intruder alarms and 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 a limited mobility and they will 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. However, a conductor allows charge to flow freely and redistribute itself within the material. The distinction between conductors and nonconductors (and it is 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. However, 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 discussed in this chapter and their units.

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 aligned. The material is now polarized and

TABLE 31.1 Terms and Units Used to Describe Dielectric Behavior

Parameter	*Definition*	*Units/value*	*Conversion factor*
C	Capacitance	F, farads	$1\,F = 1\,C/V = 1\,A^2s^4kg^{-1}m^{-2}$
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	$C \cdot m$	
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	

the polarization (or dipole moment per unit volume) is given by

$$P = Nqd \quad (31.2)$$

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.

Electronic When an electric field is applied to an atom, there is a displacement of the electrons relative to the nucleus. The electrons will 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 μ ~1.6×10^{-37} C·m. Electronic polarization is the only possible mechanism in pure materials that are covalently bonded and does not contain permanent dipoles (e.g., diamond and silicon).

Ionic This occurs when an ionically bonded material is placed in an electric field; it 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 further 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.

Dipolar This mechanism is generally uncommon in ceramics because most of the permanent dipoles cannot be reoriented without

POLARIZATION MECHANISMS

A note: In some texts you will find that the polarization mechanism occurring in $BaTiO_3$ is described as dipolar and 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).

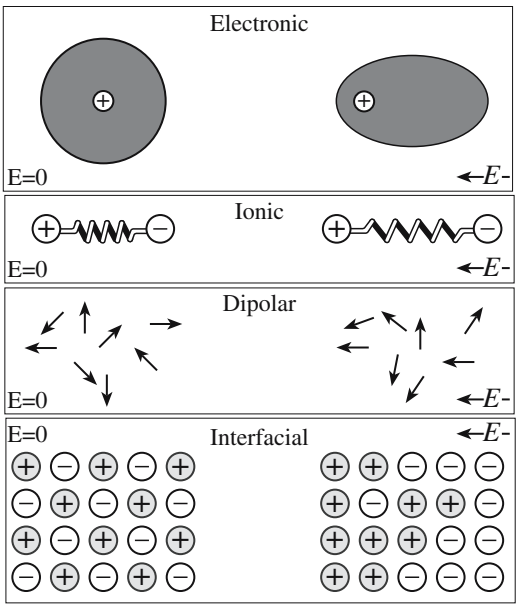


FIGURE 31.1 Illustration of the different polarization mechanisms in a solid.

destroying their crystal structure. But there are some very important exceptions and it is these materials that will form a large part of this chapter. The prototypical example is barium titanate. The 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.

Interfacial A charge may develop at interfaces (such as 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:

$$P = P_{\text{electronic}} + P_{\text{ionic}} + P_{\text{dipolar}} + P_{\text{interfacial}} \qquad (31.3)$$

Relating *P* and κ

The dielectric constant is an important materials property and 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 a capacitor plate, D_0, is proportional to the applied electric field ξ. The constant of proportionality is ε_0:

$$D_0 = Q/A = \varepsilon_0 \xi \qquad (31.4)$$

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

$$D = \varepsilon \xi \qquad (31.5)$$

D is also known as the dielectric displacement and represents the extra charge that can be stored because of the presence of the dielectric. So we can rewrite Eq. 31.5 as

$$D = \varepsilon_0 \xi + P \qquad (31.6)$$

By substituting Eq. 31.5 into Eq. 31.6 we obtain

$$\varepsilon \xi = \varepsilon_0 \xi + P \qquad (31.7)$$

By simple rearrangement we can write

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	$BaTiO_3$	3000
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 ($2MgO \cdot SiO_2$)	6.2
Cordierite ($SiO_2 + MgO + Al_2O_3$)	4.5–5.4	Mullite	6.6
High-lead glass	19	Vycor glass	3.9

$$P = (\kappa - 1)\varepsilon_0 \xi = \chi \varepsilon_0 \xi \qquad (31.8)$$

where χ is a measure of the ratio of the bound charge/free charge (i.e., P/Q). For dielectrics that polarize easily κ will be 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 such as diamond and is a combination of electronic and ionic in 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.

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 that is different for each polarization mechanism. At the relaxation frequency the dipoles will only just be 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 at a 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. It operates at the relaxation frequency of water molecules and the heat generated warms the food.

At frequencies above the relaxation frequency the dipoles will no longer be able to keep up with changes in the applied field and 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 four of the polarization mechanisms.

- 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

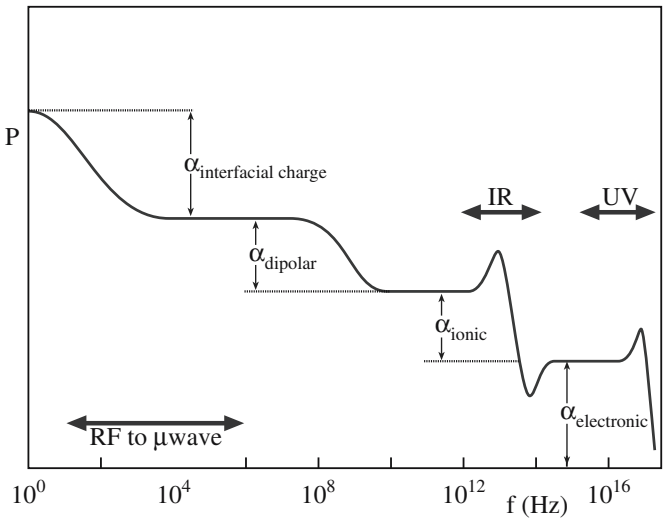


FIGURE 31.2 Frequency dependence of polarization.

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.

Dielectric Strength

A dielectric will be able to withstand a certain applied electric field strength before it breaks down and current flows. High dielectric strengths are important in applications in which the thickness of the material is going to be 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, which is one of the reasons it was used in early ceramic disk capacitors.

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

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:

$$\varepsilon = \varepsilon' - j\varepsilon'' \qquad \text{(Box 31.1)}$$

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

$$\tan\delta = \varepsilon''/\varepsilon' \qquad \text{(Box 31.2)}$$

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.

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 (‖ *c*)	0.0016
TiO_2 (‖ *a*,*b*)	0.0002
Al_2O_3 (‖ *c*)	0.0010
Al_2O_3 (‖ *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 (96 SiO_2–4B_2O_3) glass	0.0008
Soda-lime silica glass	0.0100
High-lead silica glass	0.0057

Nonlinear Dielectrics

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

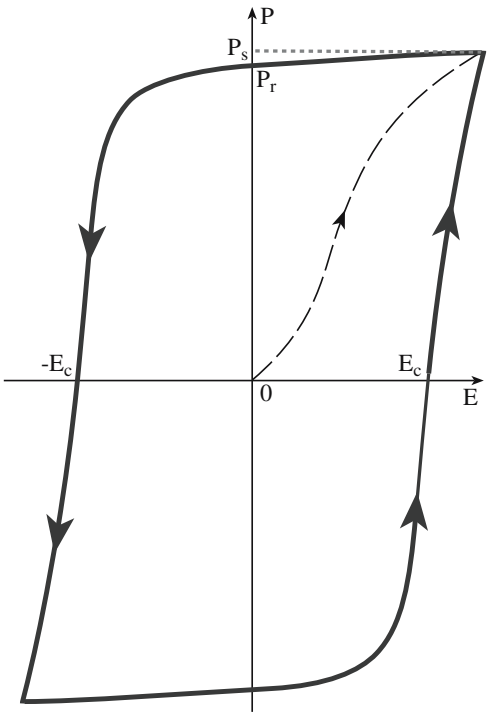


FIGURE 31.3 Hysteresis curve for a typical ferroelectric.

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

absence of an electric field. This property is the 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 will eventually occur 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.

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 a further 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

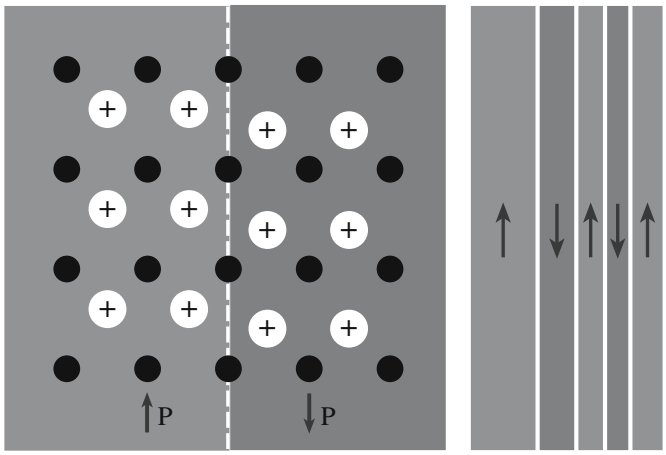
Ferroelectrics do not contain iron. The term comes from the analogy with ferromagnetism, which also does not require iron.

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

Ferroelectricity is a property that is associated not only 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 volumes of the two domain orientations. If the volumes are equal the material will 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 in which the direction of polarization



(A) (B)

FIGURE 31.4 (a) Schematic showing ionic displacements in two 180° ferroelectric domains. (b) Domain structure showing several 180° domains of different sizes.

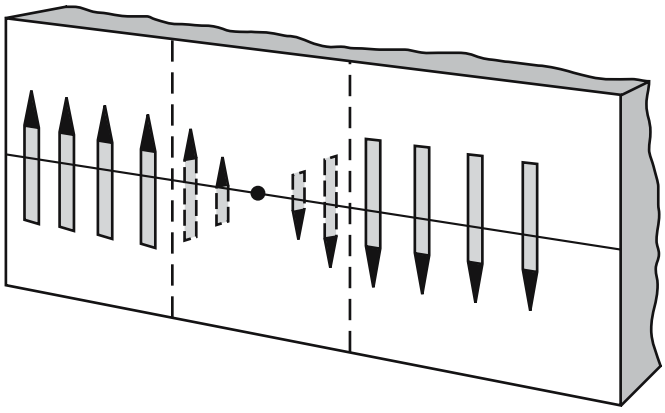


FIGURE 31.5 Illustration of a 180° domain wall. The width is ~0.2–0.3 nm.

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 are in adjacent domains at right angles.

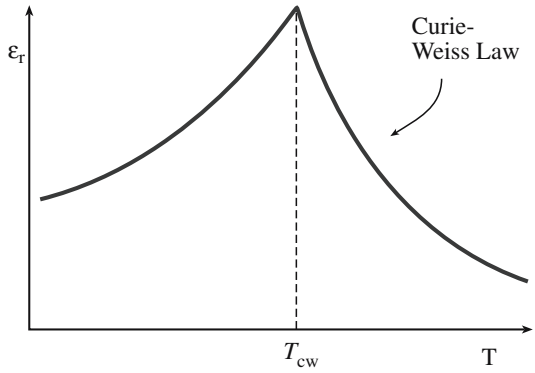


FIGURE 31.6 Relative permittivity of a ferroelectric as a function of *T*.

- 180° wall—polarization vectors in adjacent domains are antiparallel.

The wall energy is of the order of 10 mJ/m^2. This value can be compared to typical grain-boundary (GB) energies that range from 0.1 to 0.3 J/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, $PbTiO_3$, and $KNbO_3$] $T_{cw} < \theta_c$. For example, experimental measurements on polycrystalline $BaTiO_3$ have shown that T_{cw} can be more than 10°C less than θ_c. A first-order transition involves a discontinuous change in *P* with *T*.

TABLE 31.6 Curie Temperatures and Curie Constants for Several Ferroelectric Ceramics

Ceramic	*Structure*	θ_c *(K)*	*C (K)*	*Oxide*	*Structure*	θ_c *(K)*	*C (K)*
$SrTiO_3$	Perovskite	~0	7.0×10^4	$LiNbO_3$	Ilmenite	1470	
$BaTiO_3$	Perovskite	393	12.0×10^4	$LiTaO_3$	Ilmenite	890	
$PbTiO_3$	Perovskite	763	15.4×10^4	$Cd_2Nb_2O_7$	Pyrochlore	185	7.0×10^4
$CdTiO_3$	Perovskite	1223	4.5×10^4	$PbNb_2O_6$	Tungsten bronze	843	30.0×10^4
$KNbO_3$	Perovskite	712	27.0×10^4				

- For ferroelectrics that undergo a second-order transition (e.g., triglycine sulfate, Rochelle salt, and dihydrogen phosphate) $T_{cw} \sim \theta_c$. The change in P is continuous for a second-order transition.

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

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 of $r_{Ti^{4+}}/r_{O^{2-}} = 0.44$. 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, one of the 8 <111> directions, or one of the 12 <110> directions.

At temperatures greater than θ_c the Ti^{4+} has no fixed nonsymmetrical position and hence there is no permanent dipole moment. The crystal is paraelectric; it can be polarized only while it is in an applied electric field.

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

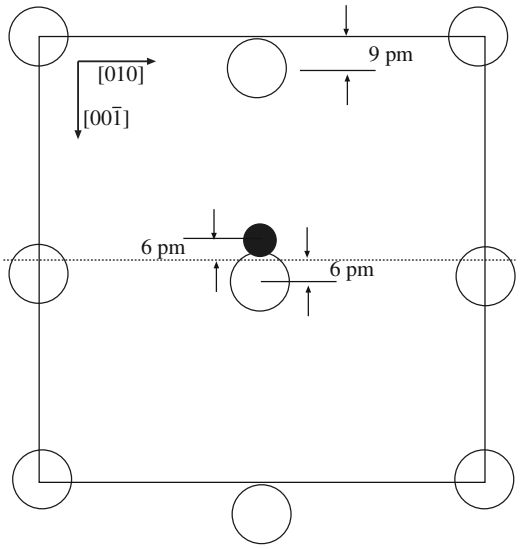


FIGURE 31.7 [100] projection of $BaTiO_3$ showing ion displacements below θ_c (not to scale).

There are other structural transformations that occur in $BaTiO_3$, these are 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 the 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.

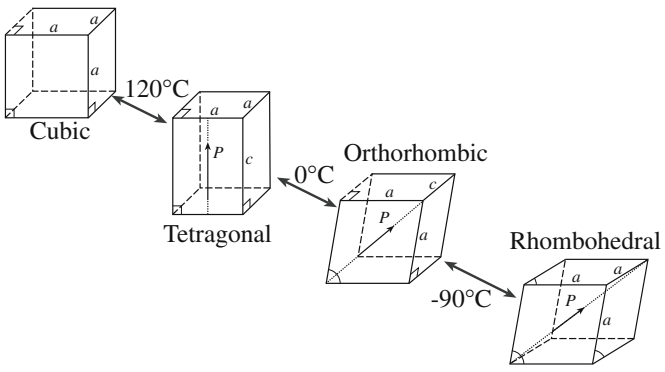


FIGURE 31.8 $BaTiO_3$ polymorphs showing direction of polarization.

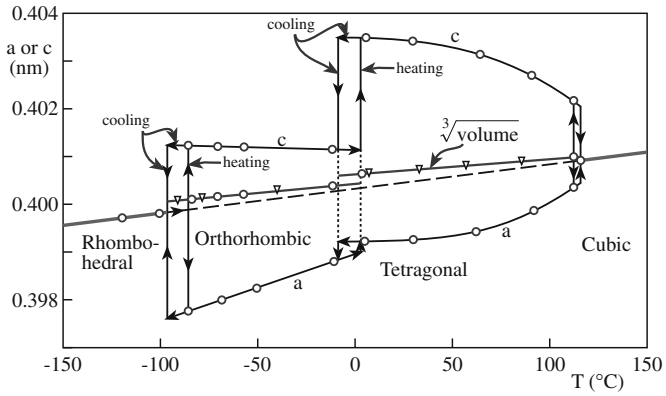


FIGURE 31.9 Experimental measurements of lattice parameters of $BaTiO_3$ as a function of *T*. Note the change in volume at each transition and the hysteresis in the lattice parameters.

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 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 the reversal of 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 since no net physical deformation is required; domains misoriented by 90° are inhibited from changing orientation by the strain that accommodates switching of *c* and *a* axes.

The almost horizontal portions of the hysteresis loop represent saturated states in which the crystal is a 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 an 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 are fatter and E_c is greater, corresponding to the larger energy required for 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 *T* range as possible

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

- A solid solution can be formed with an isostructural compound (see Section 31.4).
- The grain size can be reduced as shown in Figure 31.15.
- Mechanical stresses (compressive or tensile) in thin films can be induced because of differences in the lattice parameter between the film and the substrate, e.g., values of θ_c for $BaTiO_3$ thin films on MgO and on Pt are lower than for bulk material.

CALCULATION OF THE DIPOLE MOMENT FOR $BaTiO_3$

Using Eq. 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

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

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

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

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 a top-face O^{2-}/cell, and there are two side-face O^{2-}/cell.

The total dipole moment per unit cell is

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

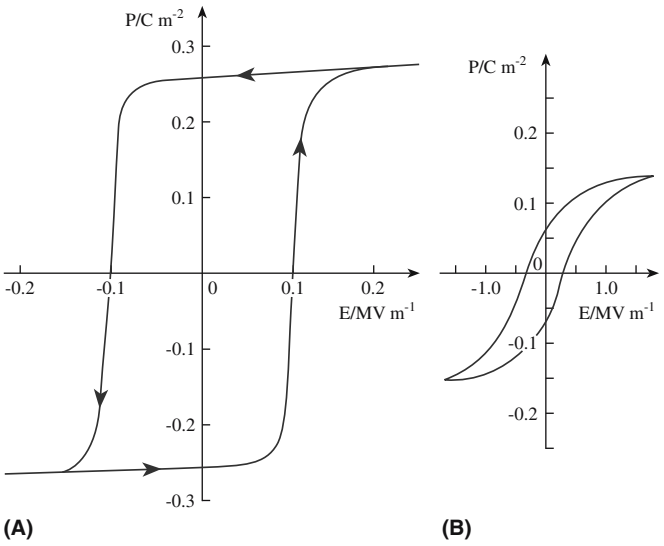


FIGURE 31.10 Hysteresis loops for $BaTiO_3$. (a) Single-domain single crystal. (b) Polycrystalline ceramic.

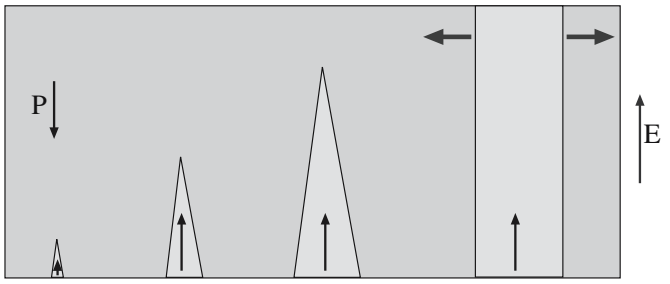


FIGURE 31.11 Illustration of the growth of a ferroelectric domain in a field ξ.

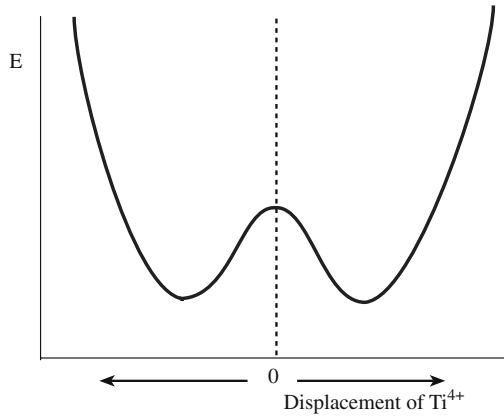


FIGURE 31.12 Potential energy wells for Ti^{4+} as a function of displacement within the octahedral site.

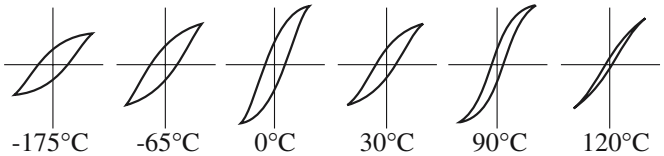
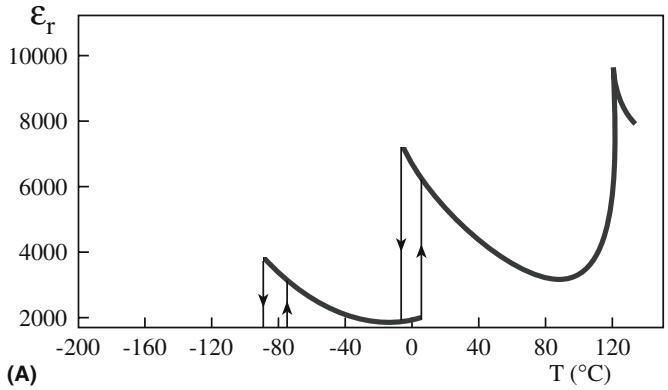


FIGURE 31.13 Hysteresis loops for $BaTiO_3$ as a function of *T*.



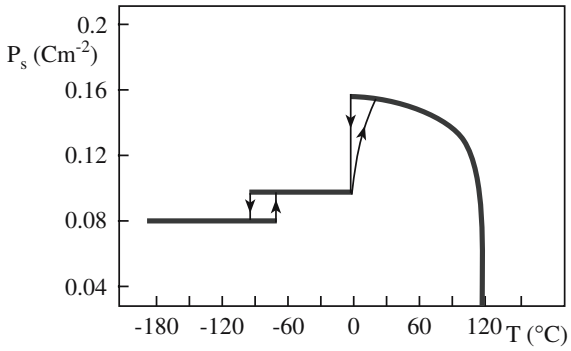


FIGURE 31.14 (a) Dielectric constant and (b) spontaneous polarization of single-crystal $BaTiO_3$ as a function of *T*. (Compare to Figure 31.9.)

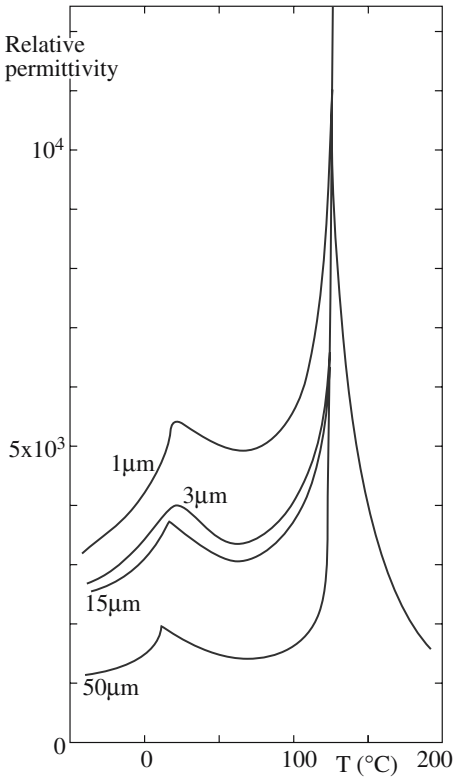


FIGURE 31.15 Effect of grain size on the dielectric constant of $BaTiO_3$.

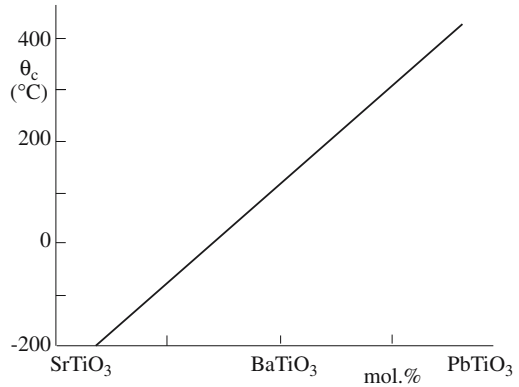


FIGURE 31.16 Effect of substitution on θ_c for $BaTiO_3$ solid solutions with $SrTiO_3$ and $PbTiO_3$.

31.4 SOLID SOLUTIONS WITH $BaTiO_3$

$BaTiO_3$ is rarely used in its pure form because, as mentioned in the previous section, 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 shifting 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 the 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, although it does not include the large number of solid-solution phases that are ferroelectric. Many ferroelectric ceramics have a perovskite structure above θ_c, but this is not a prerequisite. For example, $LiNbO_3$ has an ilmenite ($FeTiO_3$) structure and $Cd_2Nb_2O_7$ has a pyrochlore structure (the mineral pyrochlore is $CaNaNb_2O_6F$).

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
$LiNbO_3$	1200

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 shows 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 the permittivity versus temperature range, 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).

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:

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

This 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 capacitors:

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

Frequency ranges in which 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.

NOTATION FOR *C*

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

We can distinguish three basic types of ceramic capacitors:

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

Each of these types will be described separately. Film capacitors that are used in memory devices are integrated with the other circuit components. However, disc capacitors and MLCCs are discrete components.

Categories of Ceramic Capacitor Dielectric

Ceramic capacitors are generally classified into three types (1, 2, 3 or I, II, III) based on their properties.

Class 1 or *NPO* capacitors 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 the following:

- 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–100 MHz because of the stability of capacitance with temperature
- Microwave resonant cavities operating between 0.5 and 50 GHz because of their stability and low tan δ

Class 2 capacitors consist of high dielectric constant ceramics based on $BaTiO_3$. The two main subclasses are Z5U and X7R after the scheme shown in Table 31.9 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. 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 concentrate at the GBs. The compositions and properties of some Z5U and X7R dielectrics are shown in Tables 31.10 and 31.11, respectively.

Class 3 capacitors 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 while the grains themselves are conducting or semiconducting. This can be achieved in two ways:

- The ceramic is first heated to a high temperature (900–1000°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.
- 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 μm) insulating layers and the high GB area produce very high capacitances.

The properties of these dielectrics are similar to those in class 2, but their working voltages are between 2 and

TABLE 31.8 Frequency and Capacitance Ranges for Capacitor Types

Capacitor	*Maximum usable 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

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)	5700–7000	5500–6500	11,500–13,000	
Tan δ	≤0.03	≤0.03	≤0.03	

25 V. The big advantage is that simple disc capacitors can be produced with large capacitances >1 μF.

Disk Capacitors

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

The first disc capacitors used mica sheets. Mica has a very high dielectric strength (see Table 31.4) and can readily be cleaved into thin sheets. Disk capacitors are now made from $BaTiO_3$-based compositions using traditional ceramic processing methods. The powder is mixed with between 5 and 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 between 900 and 1300°C in air to produce a dense material. After sintering Ag paint is applied to the major surfaces and the discs are briefly refired at 600–800°C. Tinned copper wires are soldered to the metallized ceramic disc before the whole assembly is immersed in a polymer (usually an epoxy resin).

Disc capacitors are made using all classes of capacitor dielectric allowing a wide range of capacitances:

0.1–1000 pF using class 1 dielectrics
1000–100 000 pF using class 2 dielectrics
0.1–2 μF using class 3 dielectrics

MLCC ADVANTAGES

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

Multilayer Chip Capacitors (MLCCs)

The largest class of ceramic capacitors produced, in numbers and in value, is

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)	1600–2000	1800	1400–1500	
Tan δ	<0.025	<0.025	<0.015	

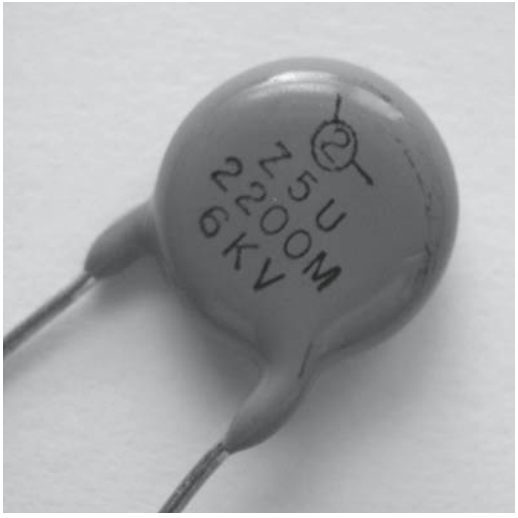


FIGURE 31.17 Ceramic disc capacitor.

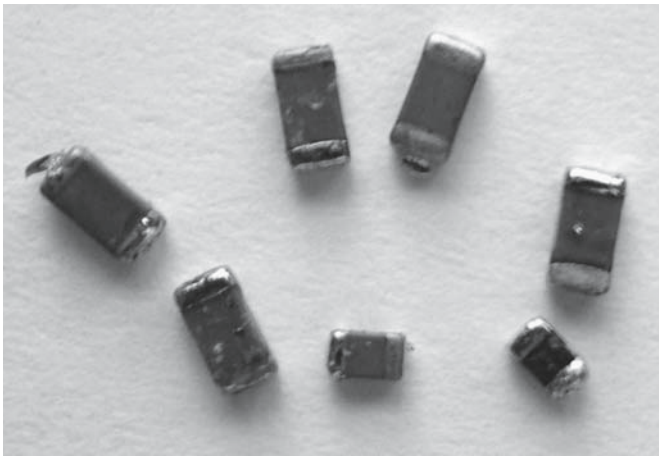
the MLCC. More than 80 billion "chips" are manufactured worldwide each year.

Figure 31.18 shows several MLCCs and a schematic of their structure. The external dimensions range from 1.25 mm × 1 mm × 1 mm thick up to 6 mm × 6 mm × 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 PFN and PMN.

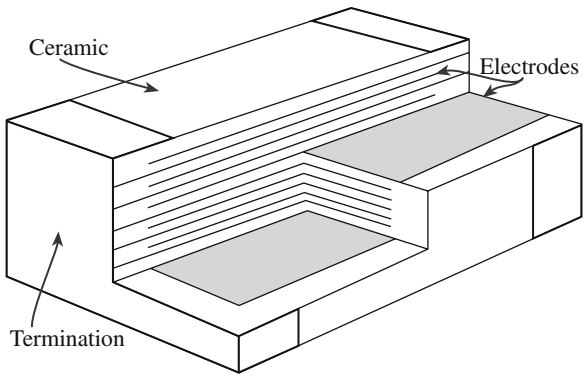
Fabricating MLCCs

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

- 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 dried sheets typically into 15-cm squares



(A)



(B)

FIGURE 31.18 (a) Ceramic MLCC. (b) Schematic showing electrode structure.

- 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 the 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 1200–1400°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 will yield 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 will yield 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, would avoid stacking and trenching, and would allow planar configurations. Such configurations are easier and cheaper to fabricate and provide high production yields.

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, which is almost always represented by ε.

Thin films of BST have been the most widely studied dielectric for ferroelectric DRAMs (FRAMs or FeRAMs). 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 is a reversible property possessed by a select group of materials that does not 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

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

The piezoelectric coefficients d and g are related by Young's modulus, $\mathcal{E}$:

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

- 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:

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

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

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

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

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

For the indirect effect

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

Since the conversion of electrical energy to mechanical energy (or vice versa) is always incomplete, k^2 is always

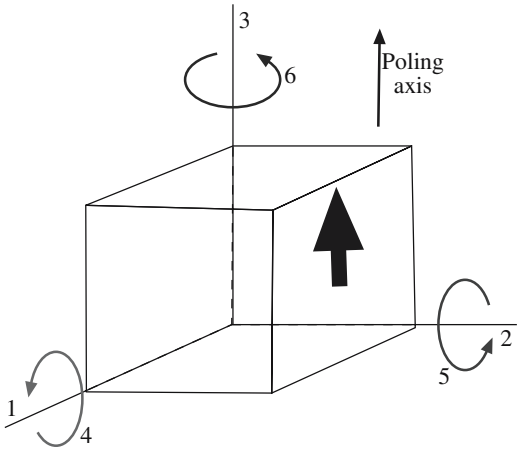


FIGURE 31.19 Notation of axes for a piezoelectric ceramic.

TABLE 31.12 Properties of Some Piezoelectric Ceramics

Material	*Piezoelectric constant C/N*	*Electromechanical coupling factor (k)*
Quartz (× cut)	$d_{21} = 2.25 \times 10^{-12}$	
	$d_{33} = 2.3 \times 10^{-12}$	0.1
$BaTiO_3$	$d_{31} = -75 \times 10^{-12}$	0.48
PZT	$d_{33} = 374 \times 10^{-12}$	0.67
Lead metaniobate	$d_{33} = 85 \times 10^{-12}$	0.42
Lithium niobate	$d_{33} = -1 \times 10^{-12}$	
	$d_{15} = 68 \times 10^{-12}$	0.4
Rochelle salt (45° × cut)	$d_{14} = 870 \times 10^{-12}$	0.78

<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.

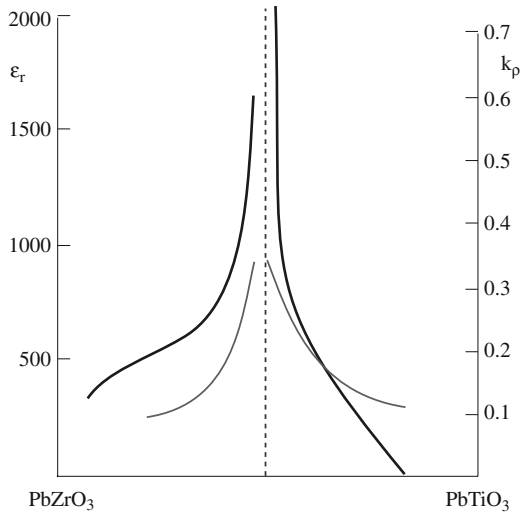


FIGURE 31.21 Dielectric constants and coupling coefficients for PZT compositions near the MPB.

31.10 LEAD ZIRCONATE–LEAD TITANATE (PZT) 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 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.

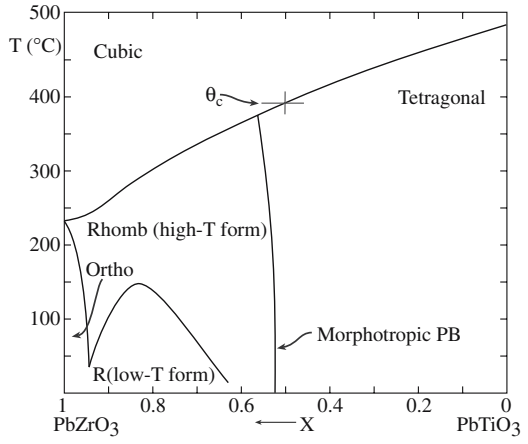


FIGURE 31.20 The PZT phase diagram.

PZT ceramics often contain dopants (in the range 0.05 to 5 at%) to modify the properties of the material for specific applications.

Examples:

1. 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 $\tan\delta$, high elastic compliance, and reduced aging. Typical applications are in areas in which high sensitivity is required, such as hydrophones, sounders, and loudspeakers.

2. 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 $\tan\delta$, low compliance, and high aging rates. Typical applications are in high-power devices such as sonar and ultrasonic transducers.

3. 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 $\tan\delta$, low compliance, and higher aging rates. These ceramics are used in high-drive applications such as torpedo guidance.

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.

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) and 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 APPLICATIONS FOR PIEZOELECTRIC CERAMICS

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

Direct effect—a voltage is produced by means of a compressive stress.

Inverse effect—an applied ξ produces small movements. In an alternating field the piezoelectric will vibrate.

Direct Effect

The first commercial piezoelectric $BaTiO_3$ devices were phonograph pickups marketed by Sonotome Corporation in the mid-1940s. These used a so-called bimorph design in which an electrode layer separated two strips of the piezoelectric material. Bimorphs are no longer used for this application because they do not produce a 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, 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. If this force is not applied quickly the voltage generated will disappear as the charge leaks away. Typical spark energies are ~3 mJ.

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 actuators. 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 microscopy (AFM) and scanning tunneling microscopy (STM).

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 (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 the fetus in the mother's womb as shown in Figure 31.22 and high-resolution imaging of 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.

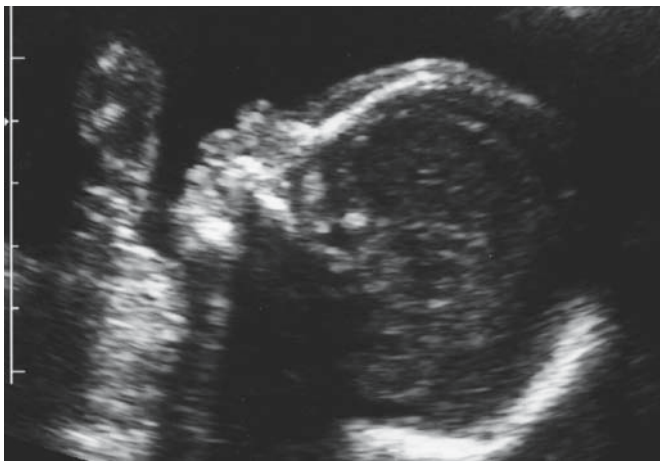


FIGURE 31.22 Medical ultrasound image using ceramic piezoelectric transducers. (Scale is in centimeters.)

31.12 PIEZOELECTRIC MATERIALS FOR MICROELECTROMECHANICAL SYSTEMS

Microelectromechanical systems (MEMS) 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) used to control the 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. The ceramic need not be both ferroelectric and piezoelectric. But if it is ferroelectric then 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.

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 uses 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 and inexpensive and give good stoichiometry control but result in poor step coverage.

31.13 PYROELECTRICITY

Pyroelectric materials exhibit a spontaneous polarization that is a strong function of temperature because the dipole moments vary as the crystal expands or contracts. This 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):	$p = 230\,\mu C\,m^{-2}\,K^{-1}$
$(Sr,Ba)Nb_2O_6$ (single crystal):	$p = 550\,\mu C\,m^{-2}\,K^{-1}$
PZT (polycrystalline):	$p = 380\,\mu C\,m^{-2}\,K^{-1}$

The electric field developed across a pyroelectric crystal can be extremely large when it is subjected

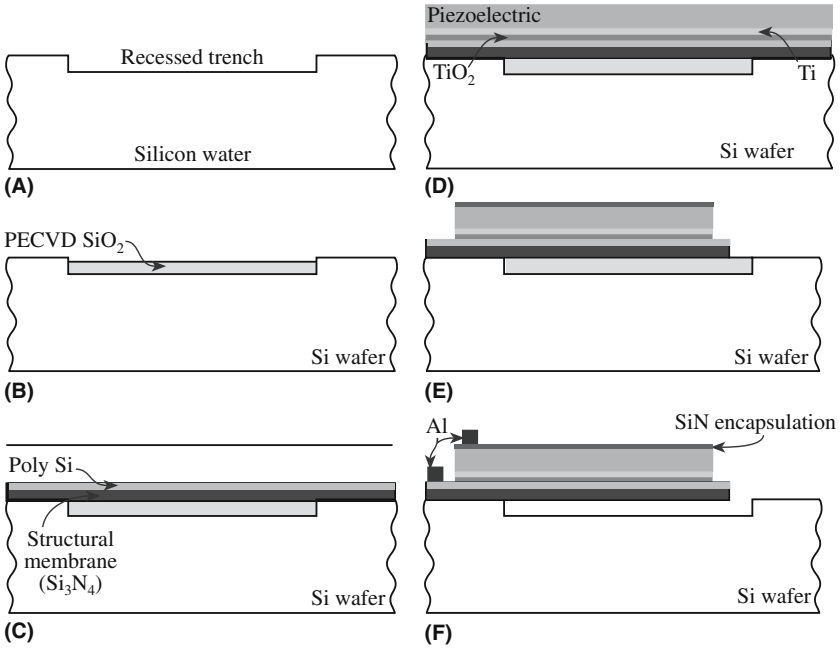


FIGURE 31.23 Steps in the production of a MEMS cantilever. (a) Create trench by etching; (b) deposit SiO_2 layer by pressure-enhanced chemical vapor deposition (PECVD); (c) deposit Si_3N_4 followed by polysilicon; (d) deposit the piezoelectric film on an electrode/diffusion barrier system; (e) pattern and etch; (f) apply metal contacts and sacrificial etch.

to a small change in temperature. A pyroelectric coefficient, p, can be defined as the change in D due to a change in T:

$$p = \frac{\partial D}{\partial T} \tag{31.21}$$

For example, a crystal with a typical pyroelectric coefficient of $10^{-4}\,C\,m^{-2}\,K^{-1}$ and $\kappa = 50$ develops a field of 2000 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 rise in temperature of less than one-thousandth of a degree can be detected. This property finds application in devices such as intruder alarms, thermal imaging, and geographic 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 Chapter 30, because dielectrics have permanent electric dipoles. If the resultant polarization is spontaneous we have ferroelectrics. This topic is essentially exclusive ceramic materials. Although some polymers are ferroelectric they do not find as wide use as ceramics. And metals cannot be ferroelectric because the charge is not localized.

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

PEOPLE IN 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) 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."

GENERAL REFERENCES

Jaffe, B., Cook, W.R., Jr., and Jaffe, H. (1971) *Piezoelectric Ceramics*, Academic Press, London. Now a little dated in view of more recent developments in the field. But the basic science remains the same.

Jona, F. and Shirane, G. (1993) *Ferroelectric Crystals*, Dover, New York. First published by Pergamon Press, Oxford, England and The Macmillan Company, New York in 1962 as Volume I in the International Series of Monographs on Solid State Physics. A comprehensive description of many types of ferroelectric crystal. Somewhat dated: the Dover edition was not updated from the 1962 Pergamon edition.

Lines, M.E. and Glass, A.M. (1977) *Principles and Applications of Ferroelectric and Related Materials*, Clarendon Press, Oxford.

Moulson, A.J. and Herbert, J.M. (1990) *Electroceramics*, Chapman & Hall, London. An outstanding and very readable coverage of the entire field of electronic ceramics including applications for capacitors. Highly recommended.

SPECIFIC REFERENCES

Smolenskii, G.A. and Agranovskaya, A.I. (1958) "Dielectric polarization and losses of some complex compounds," *Sov. Phys. Tech. Phys.* **3**, 1380. The first synthesis of PMN relaxors.

JOURNALS AND CONFERENCES DEVOTED TO FERROELECTRIC MATERIALS

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

Integrated Ferroelectrics. An international journal published by Gordon and Breach since 1992 devoted to research, design, development, manufacturing, and utilization of integrated ferroelectrics. These are devices that combine ferroelectric films and semiconductor IC chips.

Journal of Materials Science: Materials in Electronics.

WWW

www.uoguelph.ca/~antoon/gadgets/caps/caps.html

A general site on capacitors: explains that NPO is "negative-positive-zero", and emphasizes that all capacitors are polarized.

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 EIA code for a capacitor that is required to have a capacitance at room temperature that changes by no more than ±4.7% in the temperature range –55 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. 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 μC at a potential of 5 kV. The separation between the electrodes is 500 μm. Determine the plate area if the following dielectrics are used: (a) mica, (b) MgO, (c) $BaTiO_3$, (d) Al_2O_3. In each case would the dielectric be able to withstand the applied field?

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 rocksalt structure with $a = 0.421$ nm.

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