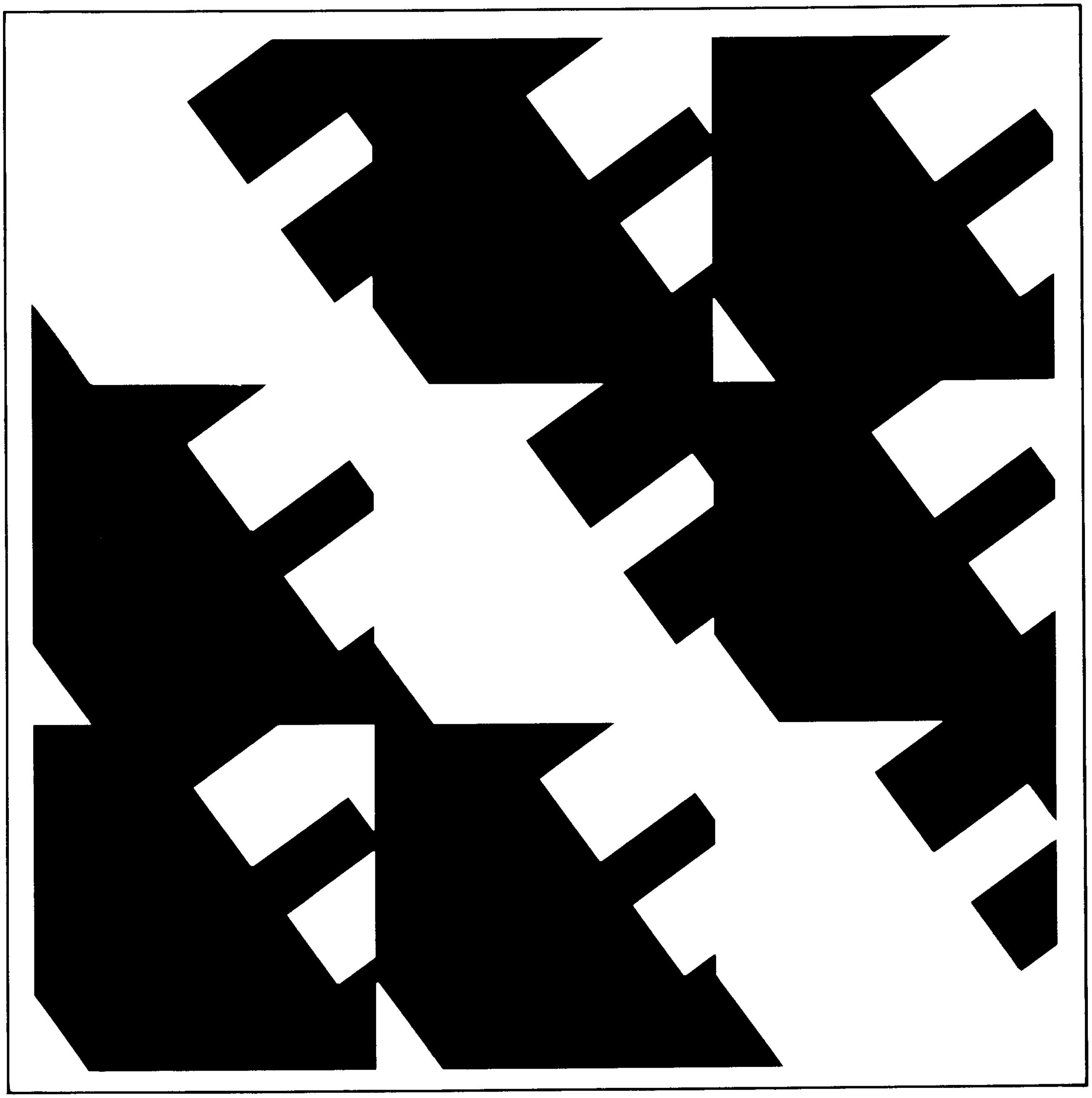
AMERICAN NATIONAL STANDARD

ANSI/IEEE Std 180-1986
(Revision of IEEE
Std 180-1962)

IEEE Standard Definitions of Primary Ferroelectric Terms



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An American National Standard

IEEE Standard Definitions of Primary Ferroelectric Terms

Sponsor

**Group on Sonics and Ultrasonics of the
IEEE Ultrasonics, Ferroelectrics and
Frequency Control Society**

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Foreword

(This Foreword is not a part of ANSI/IEEE Std 180-1986, IEEE Standard Definitions of Primary Ferroelectric Terms.)

Compared to some of the older areas of specialization found within the IEEE organization, ferroelectrics is a relatively new field. The first standard covering the definitions of ferroelectric terms was IEEE Std 180-1962 (R1971), prepared by Subcommittee 14.1 on Ferroelectric Crystals under the chairmanship of J. H. Armstrong and approved in 1962 as an IRE standard. IEEE Std 180-1962 continued in force until the publication of the present standard, which replaces it.

During the 20 years that have elapsed since the publication of the original standard, the field of ferroelectrics has enlarged substantially. New materials have been developed, new technical terms have come into use, and even new concepts have arisen. Consequently, there is a genuine need for a new standard, and the present document represents the efforts of the IEEE Committee on Ferroelectrics to meet this need.

The major emphasis in this standard is on the definition of terms. When particular terms are related to experimental measurements, the basic measuring techniques are briefly described. However, the discussions of measuring techniques are given with the intention of being recommended practices or guides rather than mandatory requirements.

Within the IEEE family of standards, there appear to be three standards that are closely related to this one: ANSI/IEEE Std 176-1978, IEEE Standard on Piezoelectricity; IEEE Std 319-1971, IEEE Standard on Magnetostrictive Materials: Piezomagnetic Nomenclature; and ANSI/IEEE Std 268-1982, American National Standard Metric Practice. The preparation of this standard was carried out with an awareness of the existence of the three related standards and an intention to keep the usage of symbols and terminology as mutually consistent as possible.

At the time of preparation of the final draft of this standard, the membership of the Ferroelectrics Subcommittee on Standards was as follows:

A. H. Meitzler, *Chairman*

J. P. Dougherty
C. E. Land
S. T. Liu
M. A. Marcus

Earlier draft versions of this standard benefited from substantial contributions by L. E. Cross, J. P. Dougherty, S. K. Kurtz, C. E. Land, and C. F. Pulvari; these five specialists in ferroelectricity deserve a large share of the credit for the existence of this standard. Other members of the parent Committee on Ferroelectrics who made notable contributions to the discussion and development of this standard include the following:

J. T. Cutchen
A. M. Glass
G. H. Haertling
R. L. Holman
W. N. Lawless
I. Lefkowitz*
R. C. Pohanka
W. A. Smith
G. W. Taylor

*deceased

The Committee on Ferroelectrics is a standing committee of the IEEE Sonics and Ultrasonics Group.

The following persons were on the balloting committee that approved this document for submission to the IEEE Standards Board:

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Contents

SECTION PAGE

FIGURES PAGE

TABLES PAGE

An American National Standard

IEEE Standard Definitions of Primary Ferroelectric Terms

1. Introduction and References

1.1 Introduction. The terms defined in this standard apply primarily to ferroelectric materials including single crystals, polycrystalline ceramics, and semi-crystalline polymers. No attempt is made in this standard to define terms related to ferromagnetic materials; but because of the coupling that exists between ferroelectric and ferroelastic behavior in some crystalline materials, ferroelastic terms are defined in one section of this standard.

1.1.1 Discussion of Ferroic Materials. The term "ferroic" originates from a unification and generalization of the concepts "ferromagnetic," "ferroelectric," and "ferroelastic." A ferroic crystal exhibits, in an attainable range of temperature and pressure, one or more of the following quantities: a magnetization, polarization, or strain that is (are) stable in the absence of any applied fields, whether magnetic, electric, or mechanical stress. Upon application of these fields or stresses, or combinations of them, one can switch the direction of the spontaneous magnetization, the spontaneous polarization, or the spontaneous strain.

Several properties of ferromagnetic, ferroelectric, and ferroelastic materials are analogous. The dielectric hysteresis of the polarization (P) versus electric field (E) characteristic of ferroelectrics and the elastic hysteresis of the strain (S) versus stress (T) of ferroelastics are both analogous to the magnetic hysteresis of the polarization (M) versus magnetic field (H) characteristic of ferromagnetics. Switching or shifts in orientation state of ferroelectric and ferroelastic crystals in general involve emergence and vanishing of different "domains" analogous to the "domain" dynamics of ferromagnetic crystals. In general, temperature-or pressure-enforced paraelectric and paraelastic phases exist for ferroelectrics and ferroelastics, respectively, just as paramagnetic phases can be induced in ferromagnetic materials by changes in temperature and pressure. It is these analogies with ferromagnetism that lead historically to the adoption of the terms " ferroelectric" [B32][1] and "ferroelastic," and finally to the important generalization "ferroic" [B2], [B4].

1.1.2 Hierarchy Among Piezoelectric, Pyroelectric, and Ferroelectric Crystals. Depending on their geometry, crystals are commonly classified into seven systems: triclinic (the least symmetrical), monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, and cubic. The seven systems in turn are divided into point groups (crystal classes) according to their symmetry with respect to a point. There are 32 such crystal classes; 20 are piezoelectric (see [1], 3.2). Piezoelectric crystals have the following property: if stress is applied along certain directions in the crystals, they develop an electric polarization whose magnitude is (within limits) proportional to the applied stress. Conversely, when an electric field is applied along certain directions in a piezoelectric crystal, the crystal is strained by an amount proportional to the applied field. Each crystal system contains at least one piezoelectric class.

Ten of the 20 piezoelectric crystal classes possess spontaneous electrical polarization; that is, they have a nonvanishing dipole moment per unit volume and are called *polar*. The ten polar crystal classes are designated 1, 2, m, 2mm, 4, 4mm, 3, 3m, 6, 6mm in the notation of Hermann and Maugin, and C_1, C_2, C_{1h}, C_{2v}, C_4, C_{4v}, C_3, C_{3v}, C_6, C_{6v}, respectively, in the notation of Schoenflies.

1.1.2.1 Polar Axis. The polar axis is a direction that is parallel to the spontaneous polarization vector.

NOTE: For crystal class m, the polar axis is in an arbitrary direction in a plane (the mirror plane). The polar axis for crystal class 1 can be in any arbitrary direction.

When a polar crystal is heated or cooled, the internal or external electrical conduction generally cannot provide enough current to compensate for the change in polarization with temperature, and the crystal develops an electric charge on its

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[1] The numbers in square brackets refer to those of the references in 1.2 or the bibliography in Section 7. The letter "B" indicates a bibliographic source.

surface. For this reason, polar crystals are called *pyroelectric* [B16], [B20].

1.1.2.2 Pyroelectric Effect. The pyroelectric effect is the appearance of an electric charge at the surface of a polar material when uniform heating or cooling changes the polarization. If the polar material is electroded and an external resistance is connected between the electrodes, the current that flows is a pyroelectric current.

NOTE: Due to the existence of free charge, the pyroelectric charge may be rapidly compensated.

All pyroelectrics are polar; ferroelectrics are a subgroup of the polar materials and, therefore, they are both pyroelectric and piezoelectric. They differ from the more general pyroelectrics principally by the reversibility or reorientability of their spontaneous polarization P_s. The reader interested in additional source material can consult [B7], [B10], [B15], [B16], [B20], [B21], [B28], [B29], and [B33].

1.1.3 Symbols and Units. A complete list of all symbols, their meanings, their dimensions in SI units, and sections or equations where certain symbols appear are given in Table 1.

Table 1
List of Symbols and Units

Symbol	Meaning	SI Units	Section or Equation
a	Area	meter^2	(3)
A	Free energy	joule/meter^3	2.4.7
C	Curie constant	K	(8)
C_x, C_p, C_i	Capacitance	farad	(2), Fig 4(a)
D_i	Electric displacement (vector)	coulomb/meter^2	(1)
E_i	Electric field (vector)	volt/meter	(1)
E_a	Electric field at field-induced ferroelectric-antiferoelectric phase transition (decreasing field)	volt/meter	Fig 10
E_c	Coercive field	volt/meter	2.3.3
E_f	Electric field at field-induced antiferroelectric-ferroelectric phase transition (increasing field)	volt/meter	Fig 10
G	Gibbs function (or free energy)	joule/meter^3	2.4.7
i_p	Pyroelectric current	ampere (coulomb/second)	1.1.2.2
i_s	Switching current	ampere (coulomb/second)	(6), Fig 8
M_s	Spontaneous magnetization (axial vector)	ampere/meter	1.1.1
P_i	Dielectric polarization (vector)	coulomb/meter^2	(1)
P_r	Remanent polarization (incremental)	coulomb/meter^2	2.3.1, Fig 7
P_R	Saturation remanent polarization	coulomb/meter^2	2.3.1, Fig 7
P_s	Spontaneous polarization (vector)	coulomb/meter^2	2.2.2
P_{sat}	Saturation polarization	coulomb/meter^2	Fig 7
Q	Charge	coulomb	(2)
Q_s	Spontaneous charge	coulomb	2.2.3
S_{ij}	Strain (second-rank tensor)		1.1.1
S_s	Spontaneous strain (tensor)		1.1.1
t	Time	second	
t_s	Switching time	second	Fig 8
T	Temperature	K or °C	
T_C	Curie point	K or °C	2.4.1
T_{ij}	Stress (second-rank tensor)	newton/meter^2	1.1.1
V	Voltage	volt	
ϵ_0	Permittivity of vacuum	$8.854 \cdot 10^{-12}$ coulomb/volt-meter	(1)
ϵ	Absolute permittivity	coulomb/volt-meter	2.2.1
κ	Relative permittivity		2.2.2
θ	Curie-Weiss temperature	K or °C	(9)
ξ	Order parameter		2.4.3

1.2 References. This standard shall be used in conjunction with the following publications.

[1] ANSI/IEEE Std 176-1978, IEEE Standard on Piezoelectricity.[2]

[2] ANSI/IEEE Std 268-1982, American National Standard Metric Practice.

[3] IEEE Std 319-1971 (R1978), IEEE Standard on Magnetostrictive Materials: Piezomagnetic Nomenclature.[3]

2. Ferroelectric Materials: Definitions and Measuring Techniques

2.1 Ferroelectric Materials. A ferroelectric material is a material that exhibits, over some range of temperature, a spontaneous electric polarization that can be reversed or reoriented by application of an electric field.

The requirement of a nonvanishing spontaneous polarization P_s is a necessary criterion, and the requirement of reversibility or reorientability of P_s is a sufficient criterion for a ferroelectric phase. Materials belonging to nonpolar crystal classes at all temperatures, and in which a metastable polar state can be induced by an applied electric field, can also show reversible pyroelectric behavior, but are not included in the definition of ferroelectrics.

The various possible stable orientations of P_s for a given ferroelectric phase are designated as *orientation states*. A ferroelectric crystal has two or more such orientation states in the absence of an electric field, and it can be switched from one to another of these states by a realizable electric field. Any two of the orientation states are identical (or enantiomorphous) in crystal structure but different in their P_s orientation at zero electric field [B3].

2.2 Polarization. Polarization is the electric dipole moment per unit volume.

NOTE: The polarization P may be expressed as the bound surface charge per unit area of a free surface normal to the direction of P.

Polarization is related to electric displacement D through the linear expression

$$D_i = P_i + \epsilon_0 E_i \qquad \text{(Eq 1)}$$

where the derived constant ϵ_0 (usually called the permittivity of free space) equals $8.854 \cdot 10^{-12}$ coulomb/volt-meter. In ferroelectric materials both D and P are nonlinear functions of E and may depend on previous history of the material. When the electric field is applied along a polar axis that is also a special axis of the prototype phase (see 2.4.2 and 2.4.8) of the crystal, this expression may then be regarded as a scalar equation, since D, E, and P all point along the same direction. When the term $\epsilon_0 E$ in the above expression is negligible compared to P (as is the case for most ferroelectric materials), D is nearly equal to P; therefore, the D versus E and P versus E plots of the hysteresis loop become, in practice, equivalent.

2.2.1 Permittivity (Small-Signal, Ferroelectric Material). Permittivity is defined as the incremental change in electric displacement per unit electric field when the magnitude of the measuring field is very small compared to the coercive electric field. The small signal relative permittivity, κ, is equal to the ratio of the absolute permittivity ϵ to the permittivity of free space ϵ_0, that is, $\kappa = \epsilon/\epsilon_0$.

NOTE: The value of the small-signal permittivity may depend on the remanent polarization, electric field, mechanical stress, sample history, or frequency of the measuring field. (Measurements are usually made at a frequency of 1 kHz or higher.)

Macroscopically, ϵ is found by measuring the capacitance. The units of permittivity are coulombs/volt-meter or farads/meter. In a ferroelectric, the measuring field or voltage must be sufficiently small in order to prevent ferroelectric domain reorientation from contributing to the permittivity.

2.2.2 Spontaneous Polarization. Spontaneous polarization is defined as magnitude of the polarization within a single ferroelectric domain in the absence of an external electric field. See also: *polarization* (2.2) and *remanent polarization* (2.3.1).

A spontaneous polarization P_s is a fundamental property of all pyroelectric crystals, although it is reversible or reorientable only in ferroelectrics. Most ferroelectric phases originate from a nonpolar prototypic phase and all of the polarization is reorientable. However, if the prototypic phase is polar, only a portion of the total spontaneous polarization may be reoriented. This reorientable or reversible portion is commonly called the spontaneous polarization.

Figures 1 and 2 illustrate an example of a case where the prototypic phase is tetragonal (4mm) (Fig 1) and the ferroelectric phase is monoclinic (m) (Fig 2), one of the two special polar groups.

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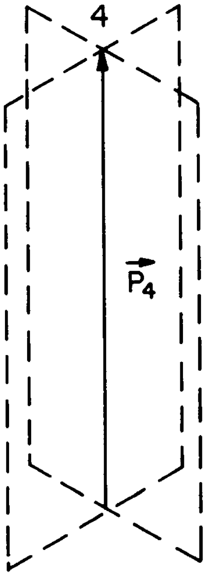
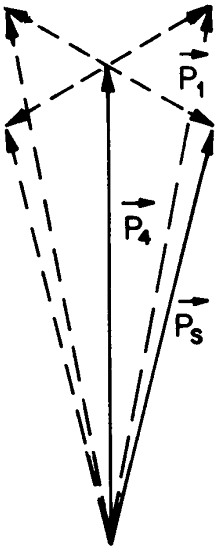
[2] ANSI publications are available from the Sales Department, American National Standards Institute, 1430 Broadway, New York, NY 10018.

[3] IEEE publications are available from the Institute of Electrical and Electronics Engineers, Service Center, 445 Hoes Lane, Piscataway, NJ 08854.



NOTE: The polar axis lies along the four-fold axis of symmetry.

Fig 1
Polar Prototype Phase, Tetragonal (4mm)



NOTE: The spontaneous polarization is not collinear with the prototype four-fold axis.

Fig 2
Ferroelectric Phase in the
Monoclinic Symmetry (m), Which Was Derived
from the Tetragonal Prototype Phase

The spontaneous polarization, P_s, in Fig 2 is composed of a switchable part, P_1, and a nonswitchable component, P_4; thus P_s is reorientable when P_1 switches between any of its four allowed states. In this example the pyroelectric vector is not collinear with the polar axis P_s, and both P_1 and P_s may independently change direction with temperature (Fig 3).

The unit cell is the smallest group of atoms within a crystal whose repetition in space generates the whole crystal. It is electrically neutral in all states of the crystal, but on this microscopic scale, P_s is associated with a polar displacement of the ionic and electronic charges within the crystalline unit cell, and this, in turn, gives rise to a microscopic electric dipole moment. In ferroelectric crystals, dipoles in adjacent unit cells are aligned in the same direction, resulting in a net P_s within a macroscopic volume (much larger than a unit cell) called a *domain*.

2.2.3 Measurement of Spontaneous Polarization. Several methods are used to measure the magnitude of P_s in ferroelectric crystals. The most common methods may be divided into two categories:

(1) Pyroelectric [B23], using charge integration as the crystal is heated to a temperature above the Curie point T_C

(2) Polarization reversal [B11] or switching [B15], using either charge integration or integration of the area under switching current i versus time t curves

Pyroelectric methods involve measurement of the charge released by the crystal in going from a fully poled (single-domain) state $\pm P_{\text{sat}}$ to the thermally depoled state $P_r = 0$. If the integrating circuit shown in Fig 4(a) is used, the voltage across the low-leakage integrating capacitor C_i is a measure of the charge released by the crystal, since

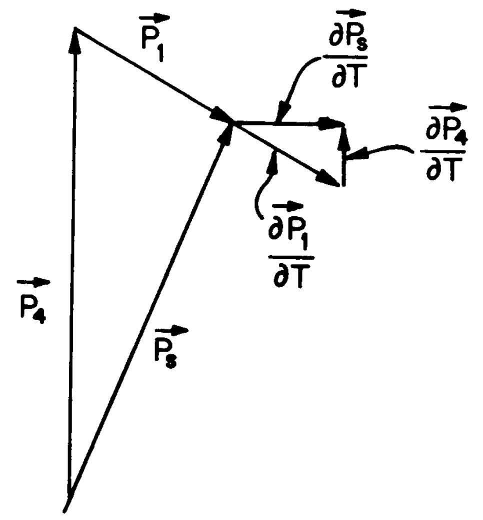
$$Q = C_i V \qquad \text{(Eq 2)}$$

provided that the capacitance of $C_i >> C_c$, where C_c is the capacitance of the crystal. The quantity P_s is then

$$P_s = Q_s / a \qquad \text{(Eq 3)}$$

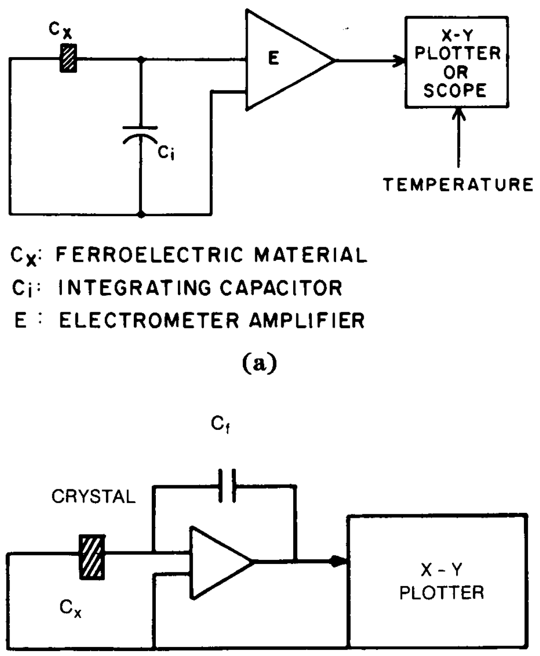
where a is the area of the crystal normal to P_s, and Q_s is the total charge stored by C_i when the sample is heated from room temperature to a temperature above T_C.

The accuracy of pyroelectric measurements depends on the dc resistivity of the crystal throughout the temperature range of the measurements. If the crystal sample resistance is less than 10^{12} Ω



NOTE: The case shown is for the monoclinic example of Fig 2. The incremental change in the pyroelectric vector, $\partial\vec{P}_s/\partial T$, is the vector sum of $\partial\vec{P}_s/\partial T$ and $\partial\vec{P}_4/\partial T$. (In most cases, the change in the pyroelectric vector lies along the same direction as the spontaneous polarization vector.)

Fig 3
Demonstration of How the Change in a Pyroelectric Vector Can Be in a Direction Different from That of the Spontaneous Polarization Vector



(a)

(b)

Fig 4
Charge Integration Methods for Measuring Spontaneous Polarization

during the measurement, the results may be inaccurate.

For crystals of low resistance, the circuit shown in Fig 4(b) will produce better results. The amplifier input impedance is so low that the crystal resistance only affects the results through the input offset current of the amplifier.

The polarization reversal or switching methods of measuring P_s involve charge integration or integration of the area under the i versus t curve while going from $\pm P_s$ to $\mp P_s$. Charge integration using dc switching fields will produce inaccurate results unless the sample dc resistance exceeds about 10^{12} Ω. See [B16] for details of a polarization reversal technique for measuring P_s, using single-voltage pulses of fixed time duration to produce polarization reversal.

Recording a hysteresis loop while switching the crystal with a low-frequency (0.1-60 Hz) sine-wave voltage provides another common method of measuring P_s [B15]. The hysteresis loop is recorded on an x-y plotter or an oscilloscope using a Sawyer-Tower circuit [B28] (shown in Fig 5) or some modification thereof. The value of P_s measured by this technique usually depends on both the frequency and amplitude of the sine-wave voltage applied. Higher accuracies are obtained at low frequencies (0.1 Hz or less) and high amplitudes (sufficient to produce peak fields at least three times the coercive field $[3E_c]$), providing the crystal dc resistance at the highest voltage is 10^{12} Ω or higher.

By the use of digital sampling techniques, one can measure P_s by the complementary methods of pyroelectric and polarization reversal techniques while recording the transient behavior. Since P_s varies with temperature, the pyroelectric discharge current on heating or cooling is given by

$$i = \left(\frac{dQ_s}{dT}\right)\left(\frac{dT}{dt}\right) = \frac{a\,dP_s}{dT}\left(\frac{dT}{dt}\right) \qquad \text{(Eq 4)}$$

if one assumes da/dT is negligible. Performing the test on cooling from above the Curie temperature will produce the maximum likelihood of complete poling. Averaging the cooling run together with a heating run will cancel contributions from conduction current since conduction current does not reverse its sign. The value of P_s at a temperature T_1 is found from

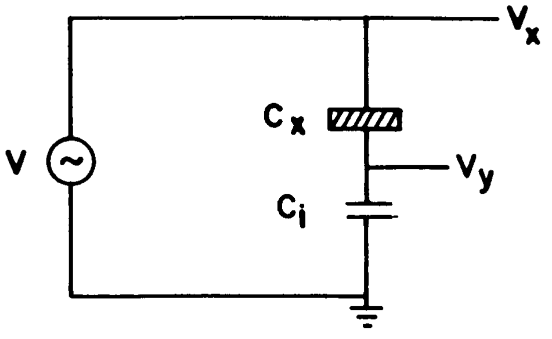


Fig 5
Sawyer and Tower Circuit for Observing Hysteresis Loops of Ferroelectric Materials

$$\int_{t_1}^{t_2} i dt = Q_s = aP_s(T_1) \qquad \text{(Eq 5)}$$

where the temperature is T_1 at time t_1 and is T_C (the Curie temperature) at time t_2.

Measuring the switching current i_s accompanying a polarization reversal (driven by a triangular voltage waveform), will provide a measurement of P_s since

$$2Q_s = \int_0^{\tau} i_s \, dt \qquad \text{(Eq 6)}$$

where τ is the period of the drive voltage. The measured i_s will contain contributions from the displacement current (the capacitance is often large and nonlinear) and the conduction current. The contributions of switching, displacement, and conduction current to the current-voltage and charge-voltage response curves are shown in Fig 6.

The value of P_s is a true material parameter and is not a function of the magnitude of the applied field. If experimental artifacts on i_s due to finite and nonlinear displacement and conduction currents appear, they can be reduced by lowering the frequency and keeping the maximum field approximately three times the coercive field in order to asymptotically approach the real value of P_s. This value of P_s should agree within experimental accuracy to the P_s determined from the pyroelectric current method.

Polarization reversal and switching techniques produce more accurate results when the crystal is initially fully poled (single domain). Crystals should be mounted so that they are free of mechanical constraints.

In addition to the more common measuring techniques enumerated previously, various optical methods may be used to measure the dependence of P_s on temperature [B24], and a comparison of methods has been made on barium sodium niobate [B30].

2.2.4 Depolarization Fields. A depolarization field is a self-generated electric field that opposes the spontaneous polarization.

In a crystal of finite dimensions there will be a discontinuity of P_s at the crystal surfaces, which gives rise to a bound polarization charge ($Q = P_s a$) of surface density P_s. This charge gives rise to an electric field called the *depolarizing field*, which opposes the spontaneous polarization. The magnitude of this depolarizing field depends on the shape of the crystal. In real materials the depolarizing field is neutralized by the flow of free charge through the crystal or from the environment. For electrically insulating crystals in an insulating environment, this process of neutralization may be very slow.

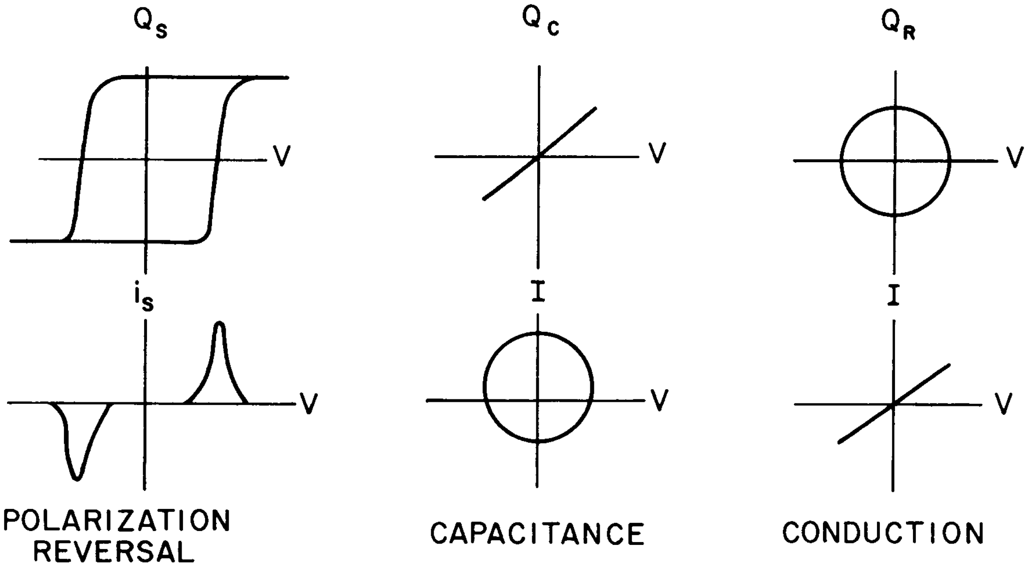
2.3 Ferroelectric Domains. A ferroelectric domain is a region of a ferroelectric crystal exhibiting homogeneous and uniform spontaneous polarization.

NOTE: An unpoled ferroelectric material may exhibit a complex domain structure consisting of many domains, each with a different polarization orientation. The direction of the spontaneous polarization within each domain is constrained to a small number of equivalent directions dictated by the symmetry of the prototype. The boundary region between two ferroelectric domains is called a domain wall. Domains can usually be observed by pyroelectric, optical, powder decoration, or electrooptic means.

In the close vicinity of domain walls, P_s is different from that in the bulk of the domain, due to the energy associated with the domain wall. The equilibrium domain structure is determined by minimization of the domain wall energy and the depolarizing energy. In a conducting ferroelectric crystal, the depolarizing fields can be neutralized by free charge so that the depolarizing energy vanishes and a single domain structure is energetically the most favorable in a perfect crystal.

The formation of a domain wall is affected by the local electric field and mechanical stresses. In crystals with many small domains, the field and stress gradients can be large enough to change the measured apparent spontaneous polarization. In small domains P_s can vary considerably across a domain, and even at the domain center may differ from that measured in a large single domain.

2.3.1 Remanent Polarization (Ferroelectric Material). The value of the polarization P_r that



POLARIZATION REVERSAL

CAPACITANCE

CONDUCTION

Fig 6
Polarization, Capacitive, and Resistive Contributions to the Hysteresis Loop for a Sinusoidal Drive Voltage Applied to the Circuit of Fig 5

remains after an applied electric field is removed is defined as remanent polarization. Remanent polarization can be measured by integrating the compensating surface charge released on heating a poled ferroelectric to a temperature above its Curie point.

NOTE: When the magnitude of this electric field is sufficient to saturate the polarization (usually $3E_c$, that is, three times the coercive electric field), the polarization remaining after the field is removed is termed the saturation remanent polarization P_R. In a single-domain ferroelectric material, the saturation remanent polarization is equal to the spontaneous polarization.

2.3.2 Poling and Switching. Poling (ferroelectric material) is the process by which a dc electric field exceeding the coercive field is applied to a multidomain ferroelectric to produce a net remanent polarization. Switching (ferroelectric material) is the process by which the remanent polarization is reversed (or reoriented) to a new value of P_r (generally equal and opposite). Switching can be produced by electric fields or mechanical stresses.

As grown, ferroelectric crystals are usually multiple domain. As a result, they may exhibit little or no net macroscopic polarization. A net polarization is imparted, and in the limit, a single-domain state is achieved by a process called *poling*. To pole a crystal, an electric field is usually applied along one of the alternative polar axes. Since the coercive field is generally minimum near T_C, common poling practice is to cool through T_C with a field applied.

As the electric field is increased in magnitude, domains favorably oriented with respect to the field direction grow at the expense of other domains. This process continues with increasing electric field until the least favorably oriented domains switch to the polar direction most nearly coinciding with the electric field direction. When no further domain reorientation can occur, the P versus E response usually becomes linear. If the linear response is extrapolated to the polarization axis ($E = 0$), the polarization value at the intersection is designated as the saturation polarization P_{sat}, as shown in Fig 7. When the electric field is removed, the mechanical boundary conditions may nucleate new reverse domains. The resulting polarization state at $E = 0$ is defined as saturation remanence P_R.

The poling process is illustrated in Fig 7 by the P versus E curve from a depoled state ($P = 0$), to saturation ($P = P_{\text{sat}}$), then to $P_r = P_R$, the saturation remanence state.

In a ferroelectric crystal initially poled to saturation remanence P_R (Fig 7), it is possible to *switch* the polarization to the opposite saturation remanence $-P_R$ by applying an electric field (equal in magnitude but of opposite polarity to the initial poling field). In most ferroelectric crystals this type of switching involves predominantly 180°

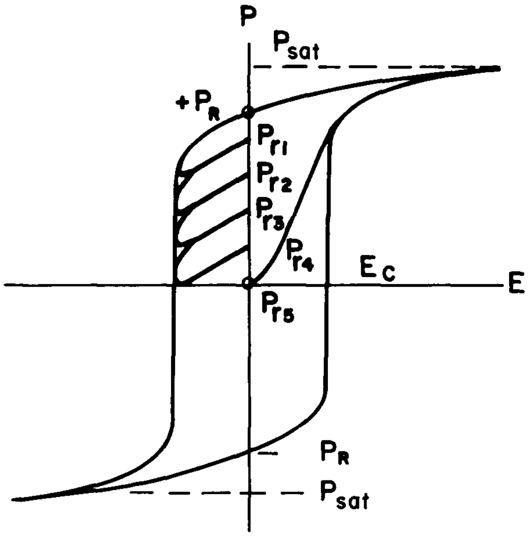


Fig 7
Spontaneous Polarization versus Electric Field Hysteresis Loop

reversal of elementary dipoles with an undetermined fraction switching by 180° via intermediate allowed crystallographic orientations. (The fractional number of dipoles switching via intermediate orientations can be estimated from strain versus polarization measurements.) In other ferroelectric crystals, for example, $Bi_4Ti_3O_{12}$, switching is effected by other than 180° dipole reversals and may involve dipole reorientations as small as a few degrees. The switching process (that is, from $\pm P_R$ to $\mp P_R$) occurs through nucleation and growth of domains that are favorably oriented with respect to the applied electric field. The domains propagate through the crystal with a direction and velocity determined by and related to the direction and magnitude, respectively, of the applied electric switching field. The domains are often related to each other by 180° (that is, equal but opposite P_s), although other orientations are allowed.

Even though each domain of a crystal can have only a single polarization state, the average of many domains allows the macroscopic polarization of some crystals to possess intermediate remanence values designated $P_{r(i)}$ in Fig 7.

If an alternating electric field of sufficient magnitude is applied to the crystal, preferably along one of the alternative polar axes, the polarization P will vary through a hysteresis loop similar to the one shown in Fig 7, although many virgin samples will often show constricted loops before opening up to a normal hysteresis.

When switching a ferroelectric with a step voltage, the time dependence of the polarization induced surface charge is given by (see [B25])

$$\frac{dQ}{dt} + \frac{t}{t_{\max}^2}\,(Q - Q_s) = 0 \qquad \text{(Eq 7)}$$

where $dQ/dt = i_s$, the switching current, and $t_{\max}$ is the time at which the switching current peaks. The value of $t_{\max}$ depends on the applied voltage as shown in Fig 8.

2.3.3 Coercive Field. The electric field required to switch the polarization from $P = \pm P_R$ to $P = 0$ is defined as the coercive field E_c (Fig 7).

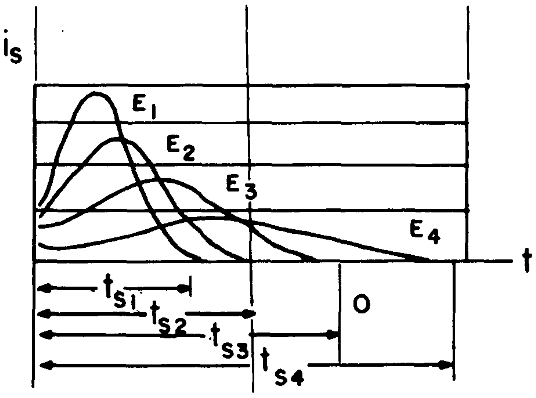
The coercive field of a ferroelectric crystal depends on its thermal and electrical history, temperature, pressure, type of electrodes, magnitude, and waveshape of the applied switching voltage (that is, E_c increases as a function of the rate of polarization reversal).

2.3.4 Differential Permittivity (Ferroelectric Material). The slope of the hysteresis loop (electric displacement versus electric field) at any point.

Differential permittivity is usually measured at low frequency (60 Hz) due to the self-heating produced on cycling through a hysteresis loop. The value of differential permittivity is often different from the small-signal permittivity measured under equivalent bias conditions.

2.4 Phase Transition (Ferroelectric Material). The phase transition of a ferroelectric material is defined as a change in the crystal structure, usually occurring at a well-defined temperature, which alters the orientation or magnitude, or both, of the electric polarization.

Fig 8
Variation of Switching Current Transient with Field ($E_1 > E_2 > E_3 > E_4$)



2.4.1 Ferroelectric Curie Point, T_C. The ferroelectric Curie Point, T_C, is defined as temperature at which a ferroelectric material undergoes a structural phase transition to a state where spontaneous polarization vanishes.

NOTE: The Curie point is determined at zero applied field.

At the Curie point, the small signal permittivity and the piezoelectric coefficients usually exhibit a peak. As a rule, the low temperature phase is ferroelectric and the high temperature phase paraelectric. In some materials, however, the high temperature phase may be a polar phase of higher symmetry than the ferroelectric phase. The Curie point T_C should not be confused with the Curie-Weiss temperature θ, which is used to define the paraelectric phase.

2.4.2 Proper Ferroelectric. A proper ferroelectric is a ferroelectric in which the polarization is the primary order parameter.

In most ferroelectric crystals, the ferroelectric phase may be regarded simply as a polarized version of a higher symmetry prototype phase, which is often the paraelectric phase. The additional changes of optical, elastic, piezoelectric, and other properties that occur in the ferroelectric phase may be regarded as indirect consequences of the appearance of the spontaneous polarization, P_s, and are related to it by normal coupling parameters. Microscopically, the ordering displacements that occur below T_C are consistent with the appearance of a homogeneous electric polarization P (that is, P_s is called an effective *order parameter* with which to describe the phase change at T_C). Ferroelectric crystals of this type are called *proper*. $BaTiO_3$ is an example of a proper ferroelectric.

2.4.3 Improper Ferroelectric. An improper ferroelectric is a ferroelectric in which the polarization is not the primary order parameter.

In certain ferroelectric crystals, however (for example, $Gd_2(MoO_4)_3$), the polarization, P_s, is but one consequence of a more general system of displacements or changes in order from the higher symmetry prototype; thus P_s is no longer an effective order parameter with which to describe the phase transition at T_C. In an improper ferroelectric phase transition the reduction in symmetry that occurs at the phase transition cannot be accounted for entirely by the appearance of the spontaneous polarization alone.

If a new order parameter ξ (whose value is not necessarily a single measurable quantity, but can be a set of several such quantities) couples only to the first power of the polarization components, a nonzero value of ξ in the ordered lower temperature phase will be accompanied by a nonzero polarization P_s; in addition, if the displacement system has more than one orientation possible in the lower temperature form, more than one orientation of P_s will occur, and if the displacements are small enough, reorientations will occur between these states, making ferroelectricity possible.

In such a crystal, however, since there is a zero value of ξ above T_C, the onset of the ferroelectric phase is not preceded by a rise in the dielectric susceptibility, and no Curie-Weiss behavior occurs in this region. For this special case where the dielectric behavior is normal above T_C, the material is ferroelectric below T_C, and where the volume of the primitive unit cell changes at T_C, the term *improper ferroelectric* has been used.

In present usage, *improper* has been confined to those cases where the dielectric behavior above a ferroelectric transition is normal; however, more subtle cases are possible in which P_s again is not a proper order parameter, but in which the influence of the dominant displacement systems may couple more directly to the dielectric susceptibility.

2.4.4 Order Parameter (ξ). A parameter, or functionally related set of parameters, that can describe the reduction in symmetry occurring at a phase transition from a nonferroic phase to a ferroic phase is defined as an order parameter.

In a proper ferroelectric, P_s is the order parameter, and in a proper ferroelastic, spontaneous strain S_s is the order parameter. In ferroic crystals with more than one spontaneous quantity (M_s, P_s, S_s), the order parameter is not necessarily any single measurable quantity but may be a function of M_s, P_s, and S_s.

2.4.5 Paraelectric Phase. The paraelectric phase encompasses the range of temperature or pressure over which the permittivity exhibits Curie-Weiss behavior.

A ferroelectric material is said to be *paraelectric* at temperatures above the Curie point T_C if the small-signal relative dielectric permittivity κ is characterized by a Curie-Weiss behavior as shown in Fig 9; that is

$$\kappa = C/(T-\theta) \qquad \text{(Eq 8)}$$

where

C = Curie constant
T = Absolute temperature in K
θ = Curie-Weiss temperature in K

In a paraelectric phase, $d\kappa/dT < 0$, and $1/\kappa$ versus T is linear, and it approaches or it may be extrapolated to zero at the Curie-Weiss temperature θ;

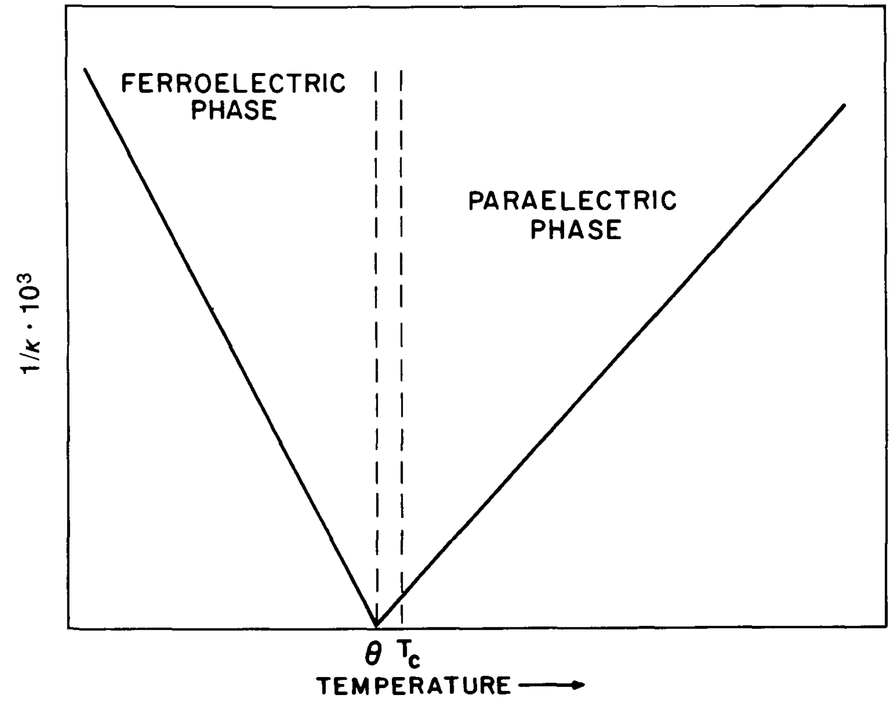


Fig 9
Plot of $1/\kappa$ versus T, Demonstrating Curie-Weiss Behavior

as shown in Fig 9, θ is always $\leq T_C$ and generally within a few degrees of T_C. A paraelectric phase always has a higher crystallographic symmetry; it usually occurs at higher temperatures than a neighboring ferroelectric phase; and it is usually but not always nonpolar. Within a paraelectric phase, an electric polarization may be induced by application of an electric field, and if a ferroelectric phase is energetically close, ferroelectricity can be field-induced by an electric field of sufficient magnitude [B15].

Some crystals with phase transitions from ferroelectric to nonpolar phases do not exhibit a Curie-Weiss behavior of the dielectric permittivity. The high temperature phase in this case is sometimes called *orthoelectric* [B12]. In contrast with paraelectric phases, the dielectric behavior is normal, the phases are always nonpolar (although polarization may be induced by application of an electric field), and they may occur in nonferroelectric as well as ferroelectric crystals. Examples of crystals that have only a minor change in dielectric permittivity at the phase transition are the improper ferroelectrics $Gd_2(MoO_4)_3$ and $Fe_3B_7O_{13}I$.

2.4.6 Curie-Weiss Temperature (Ferroelectric Material). The Curie-Weiss temperature of a ferroelectric material is defined as the intercept θ of the linear portion of the plot of $1/\kappa$ versus T, in the region above the ferroelectric Curie point, where κ is the small-signal relative dielectric permittivity measured at zero bias field along the polar axis, and T is the absolute temperature.

NOTE: In many ferroelectrics, κ follows the Curie-Weiss relation

$$\kappa = \epsilon/\epsilon_0 = C/(T - \theta) \qquad \text{(Eq 9)}$$

where

ϵ = small-signal absolute permittivity
ϵ_0 = permittivity of free space ($8.854 \cdot 10^{12}$ coulomb/voltmeter)
C = Curie constant
θ = Curie-Weiss temperature

The Curie-Weiss temperature, θalways less than or equal to the Curie point T_C and generally within a few degrees of T_C.

2.4.7 Order of the Phase Transitions. Ferroelectric phase transitions are said to be of first-order when the spontaneous polarization changes abruptly at the Curie point. Second-order phase transitions are characterized by a smooth disappearance of P_s at the Curie point. Barium titanate is an example of a ferroelectric with a first-order phase transition; triglycine sulfate (TGS) is a material with a second-order transition.

The Curie-Weiss behavior in the paraelectric phase is often used to find the order of the phase transition. The slope of $1/\kappa$ versus T in the paraelectric phase is ⅛ or ½ of the slope in the ferroelectric phase for first- and second-order phase transitions, respectively. Deviations from ideal behavior are common; the behavior of $1/\kappa$ versus T should be considered illustrative rather than definitive.

In general, a phase transition is defined in at least two respects: thermodynamic and structural. The order of the phase transition provides a useful thermodynamic characterization; the type of transition, that is, displacive or order-disorder, provides information concerning structural properties.

A first-order transition occurs when there is a discontinuity between those properties of the two phases at equilibrium, for example, enthalpy, entropy, volume, polarization, and so forth, which are described by first derivatives of the Gibbs function, G, or the free energy, A, with respect to pressure or temperature. An easily measurable property, the saturation remanent polarization, P_R, is discontinuous with respect to temperature or pressure at a first-order phase transition.

A second-order transition occurs when the first derivatives of G or A are continuous at the transition point; but the second derivatives, for example, thermal expansion, compressibility, and specific heat, are discontinuous. The saturation remanent polarization P_R is continuous with respect to temperature and pressure at a second-order transition point.

2.4.8 Prototype Phase. In general, a ferroelectric (or ferroelastic) phase of a crystal can be regarded as a slight modification of a higher symmetry nonferroelectric (or nonferroelastic) phase of the same crystal, which is designated the initial [B29] or *prototype phase* [B3]. The prototype phase may be real (for example, the paraelectric phase of a ferroelectric crystal) or it may be conceptual only. (For example, the tetragonal, orthorhombic, and rhombohedral phases of barium titanate, which are all ferroelectric, are all derivable from a common prototype phase that is cubic.) However, guanidine aluminum sulfate hexahydrate (GASH) is a ferroelectric crystal that decomposes at a temperature lower than the Curie point; therefore, the prototype phase for this material is only conceptual. Similarly, the prototype phase is only conceptual for a material like polyvinylidene fluoride (PVF_2), which melts at a temperature below its Curie point.

A real prototype phase exists for most ferroelectric crystals and borders on the ferroelectric phase at the Curie point, T_C, or may be separated from the latter by other phases [B29]. If more than one ferroelectric phase exists for a given crystal (for example, $BaTiO_3$), then the prototype phase is the same for all of the ferroelectric phases. The prototype phase may be either polar or nonpolar, depending on the symmetry of the ferroelectric phase.

2.4.9 Types of Phase Transitions. When a material is cooled through T_C, the phase transition that occurs may be either displacive or order-disorder, or it may be a combination of both types. If the high temperature phase of the ferroelectric is different from the prototype and not derivable from the prototype, an order-disorder component is possible, with no restriction on the proportion of this component [B1].

2.4.10 Diffuse Ferroelectrics. Diffuse ferroelectric single crystals or polycrystalline solid solutions are materials whose small-signal permittivity, when measured as a function of temperature, indicates by its width a broad or diffuse phase transition between the ferroelectric and nonferroelectric phases [B31]. These materials exhibit weak ferroelectric properties in the temperature range of the diffuse phase transition. Diffuse ferroelectrics are noted for their almost anhysteretic P versus E behavior and have been called weak or dilute ferroelectrics, *slim-loop* materials [B18], penferroelectric [B22], and quasiferroelectric [B9] or alpha-phase [B17] materials.

3. Antiferroelectric Materials

Antiferroelectric crystals exhibit structural phase changes and anomalies in dielectric permittivity as well as some other properties similar to ferroelectrics. However, antiferroelectric crystals have zero net switchable dipole moment per unit cell, and consequently they exhibit no macroscopic polarization hysteresis in their low-signal P versus E characteristics. This behavior is usually the result of antiparallel alignment of elementary dipoles, for example, $PbZrO_3$.

Many antiferroelectric crystals have a ferroelectric phase comparable in free energy; the ferroelectric phase can be induced by the application of an electric field of sufficient magnitude. The threshold field required to induce a ferroelectric phase is designated E_f as shown in Fig 10. If after field-

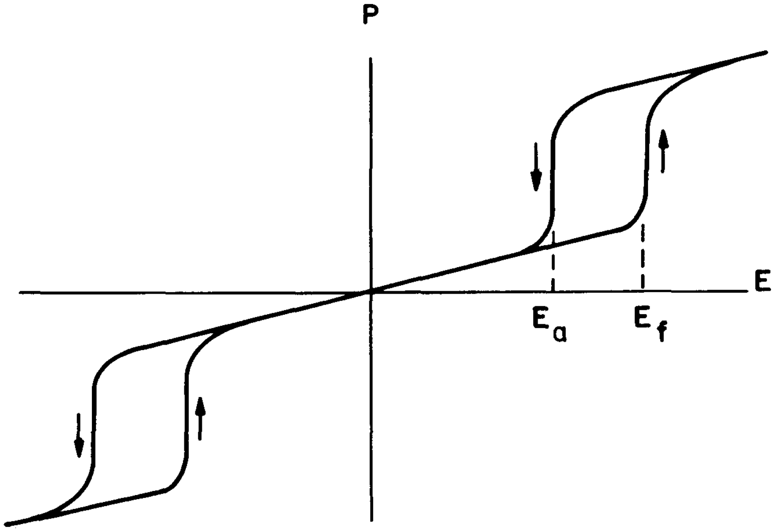


Fig 10
Polarization-Electric Field Characteristic for an Antiferroelectric Material

inducing the ferroelectric phase, the magnitude of E is reduced, the crystal returns to its initial antiferroelectric phase. The field at which the latter transition occurs is designated E_a (see Fig 10).

4. Ferroelectric Ceramics and Ferroelectric Polymers: Definitions and Measuring Techniques

4.1 Ferroelectric Ceramics. A ceramic is, in general, any inorganic, nonmetallic, ordered or disordered material. A ceramic is commonly typified by polycrystallinity and the unique properties associated with grain boundaries.

A ferroelectric ceramic is typically a sintered polycrystalline material comprising an aggregate of ferroelectric single crystal grains (or crystallites). Each ceramic grain has properties similar to a ferroelectric single crystal, with the possible exception of grains with major dimensions $<< 1$ μm.

NOTE: Both single crystal and sintered materials are, strictly speaking, ferroelectric ceramics even though they are often separated in common usage of the terms.

Because of the imperfect alignment of the crystallographic axes of grains within the aggregate, the macroscopic properties of a ceramic differ significantly from those of the constituent crystallites. For example, the macroscopic symmetry properties of all poled ceramics are essentially the same. The symmetry elements of poled ceramics are an axis of rotation of infinite order in the direction of polarization and the infinite set of all planes parallel to that axis as reflection planes (that is, conical symmetry). The set of independent elastic, piezoelectric, dielectric, and electrooptic constants that differ from zero is the same as for the dihexagonal polar class (6mm = C_{6v}) of cylindrical symmetry [B13].

Ceramic grain dimensions may vary from less than 0.5 μm to more than 40 μm, depending on the chemical composition and method of preparation. The two principal preparation processes are sintering at atmospheric pressure and sintering at elevated pressure (hot-pressing). In general, the ferroelectric, ferroelastic, dielectric, piezoelectric, and electrooptic properties of a ceramic can be controlled within much smaller tolerances if the material is hot-pressed rather than atmosphere sintered [B14], [B18].

4.2 Ferroelectric Polymers. A ferroelectric polymer is, typically, a semicrystalline polymer with a large net dipole moment per unit volume. These materials exhibit a spontaneous electric polarization that can be reversed by the application of a strong electric field (0.1-0.5 MV/cm) and also exhibit piezoelectric and pyroelectric behavior. Examples of ferroelectric polymers include polyvinyl fluoride (PVF), polyvinylidene fluoride (PVF_2), and copolymers of vinylidene fluoride with vinyl trifluoroethylene or tetrafluoroethylene. The copolymers of vinylidene fluoride with trifluoroethylene exhibit Curie temperatures in the range of 50-160 °C. The higher trifluoroethylene content materials (greater than 55 mol% VF_3) have a second-order transition at lower Curie points; while the materials with higher vinylidene fluoride content (greater than 65 mol% VF_2) have a first-order transition at higher Curie points.

4.3 Poling and Switching. In principle, the poling process in ferroelectric ceramics and polymers is the same as in single crystals. A practical difference exists because the polar axes of the ceramic grains or polymer crystallites are randomly oriented and can never be perfectly aligned with an applied electric field. The result is that for a given ferroelectric material, the measured P_R is always smaller in the ceramic, polycrystal, or semicrystalline polymer than for a single crystal. For example, the theoretical expected maximum P_R of a ceramic with respect to a single crystal depends on the crystal class of the individual grains and is calculated based on an averaging over the orientations of all the grains [B14], [B18], [B26]. The results of calculations for four common ferroelectric crystal phases expressed as the ratio of $\bar{P}$ (ceramic)/P_s (crystal) are given in Table 2.

In an individual grain of a ferroelectric ceramic, switching occurs in a manner similar to that described for crystals. Because the crystallographic axes of grains are randomly oriented in a ceramic, the type of switching that occurs in a given grain depends on the component of the switching field acting on the elementary dipoles of that grain. On a macroscopic scale, polarization reversal (that is, switching from $\pm P_R$ to $\mp P_R$) is achieved by averaging the effects of domain reorientations occurring in individual grains over the volume of the ceramic.

In general, intermediate remanence states $P_{r(i)}$ (see Fig 7) in ceramics are more stable than in single crystals.

4.4 Ferroelectric Glass-Ceramics. A multiphase solid containing ferroelectric crystal grains and other phases, one of which must be a glass. Typical grain sizes vary from 10^{-2}-50 μm, depending on chemical composition and nucleation-crystallization conditions.

The principal fabrication process of a glass-ceramic [B5], [B6], [B19] has three steps:

(1) A molten solution is formed of the ferroelectric and the glass-forming constituents

(2) The melt is rapidly quenched to form a vitreous body

(3) Controlled devitrification is accomplished by annealing

A chief advantage of a glass-ceramic is a wide range of formability, depending upon the viscosity-temperature behavior prior to devitrification.

5. Ferroelastic Materials: Definitions

5.1 Ferroelastic Crystals. A ferroelastic crystal is one that has two or more orientation states in the absence of mechanical stress and electric field, and can be shifted from one to another of these states by a mechanical stress.

5.2 Spontaneous Strain. Spontaneous strain is defined as the summation of all the strains necessary to convert a ferroelastic crystal from the nonferroelastic prototype state to one of the ferroelastic orientation states. The prototype state, by definition, has zero spontaneous strain.

A ferroelastic crystal can be switched from one ferroelastic orientation state to another by mechanical stress. Any two of the states are identical or enantiomorphous in crystal structure but different in mechanical strain tensor at zero mechanical stress (and at zero electric field) [B3].

5.3 Ferroelastic Domains and Switching. Switching in ferroelastic crystals is generally expected to involve nucleation, growth, and vanishing of ferroelastic domains. The relationship between strain S and stress T in the switching process is generally square-hysteretic as shown in Fig 1 of [B3].

Table 2
Relationship Between Ideal Single Crystal Polarization P_s and Expected Ceramic Polarization $\bar{P}$

Crystal Phase	Polarization Directions	Number of Equivalent Directions	$\frac{\bar{P}}{P_s}$
Monoclinic	[100], [100]	2	0.5
Tetragonal	<100>	6	0.831
Orthorhombic	<110>	12	0.912
Rhombohedral	<111>	8	0.866

The two (or more) orientation states of S for the ideal crystal are thermodynamically equivalent and of equal stability. Within a ferroelastic domain, S is homogeneous and uniform throughout the volume, except in the close vicinity of domain boundaries and of the surfaces of the crystal. Domains differ from one another primarily in size and in the orientation of S, providing the crystal is in a stable, single ferroelastic phase.

5.4 Paraelastic Phase. This phase encompasses the range of temperature in which the elastic compliance exhibits Curie-Weiss behavior.

A paraelastic crystal is defined by analogy with paraelectric crystals as a crystal in which mechanical strain S is a single-valued function of mechanical stress T, whose elastic compliance exhibits an obvious Curie-Weiss behavior with temperature over some given temperature range, and which at some critical temperature T_C undergoes a phase transition to a ferroelastic phase. Crystals that clearly have a paraelastic phase include the metallic alloys Nb_3Sn, In-Th, Au-Zn-Sn, and lithium ammonium tartrate.

6. Coexistence of Ferroic Properties

Ferroic crystals can exist that are both ferroelectric and ferroelastic. The equilibrium states of these two properties can coexist in four ways:

(1) All of their states differ both in polarization vector and strain tensor when referred to a common axial system

(2) All states are different in polarization vector and at least one state (but not all) is different in strain tensor

(3) All states differ in strain tensor and at least one state (but not all) is different in polarization vector

(4) At least one state (but not all) is different in polarization vector and at least one state (but not all) is different in strain tensor

Crystals of type (4) may be regarded as partially ferroelectric and partially ferroelastic (for example, the room temperature phase of $NaBa_2NbO_5$). Crystals of types (2) and (3) may be regarded as fully ferroelectric-partially ferroelastic and fully ferroelastic-partially ferroelectric, respectively. Crystals of type (1) that are both ferroelectric and ferroelastic in the original sense of the definitions may be said to be both fully ferroelectric and fully ferroelastic, for the sake of comparison with types (2) and (3) [B2].

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