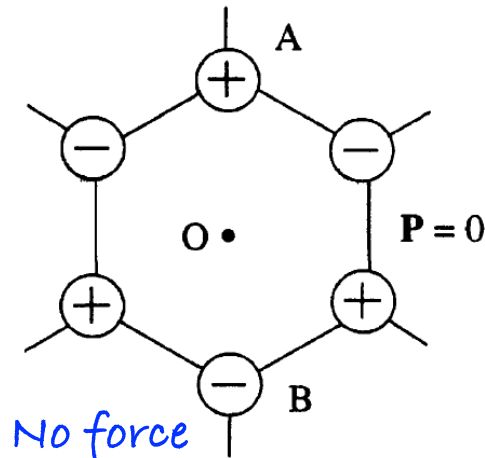


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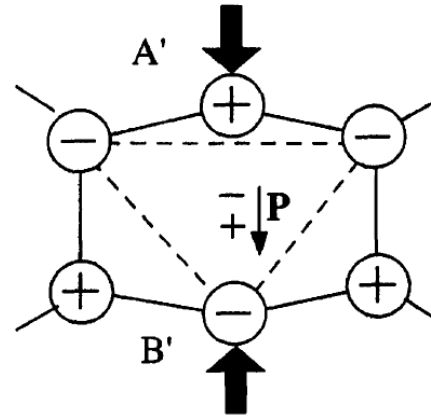
Wednesday, Oct. 23, 2024

Piezoelectricity, Ferroelectricity and Pyroelectricity

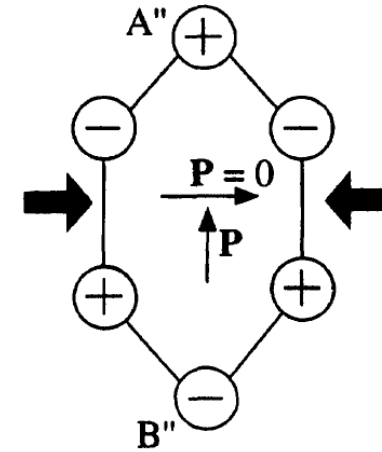
Piezoelectricity



No force
Regular geometry
No dipole moment
(a)



Force in y direction
Dipole moment in y dir
(b)



Force in x direction
Dipole moment in y dir
(c)

A hexagonal unit cell has no center of symmetry. In the absence of an applied force, the centers of mass for positive and negative ions coincide. Under an applied force in the Y direction, the centers of mass for positive and negative ions are shifted, which results in a net dipole moment, P , along y . When the force is along a different direction, along x , there may not be a resulting net dipole moment in that direction though there may be a net P along a different direction (y).

Generally, an applied stress in one direction can give rise to induced polarization in other crystal directions. Suppose T_j is the applied mechanical stress along some j direction and P_i is the induced polarization along some i direction; then the two are linearly related by

$$P_i = d_{ij} T_j$$

Piezoelectric Coefficients

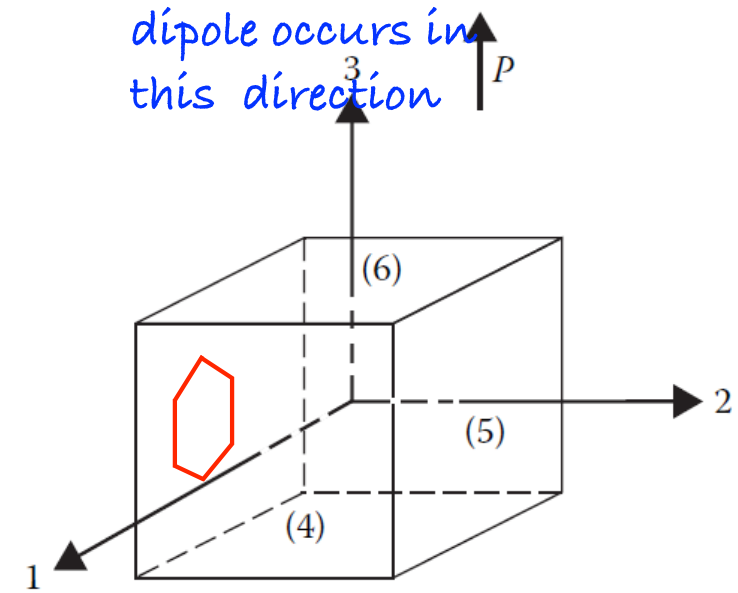
The piezoelectric coefficient relates the electric charge generated per unit area with an applied mechanical force.

Conventionally the tensile or compressive forces are applied along directions 1, 2, and 3, also designated as the x-, y-, and z-axes. Planes designated as 4, 5, and 6 are for the shear stresses. Direction 3 is considered the poling direction.

$$d = \text{Strain developed} / \text{Applied field} = \text{Charge density} / \text{Applied stress}$$

The coefficient d_{33} is one of the piezoelectric charge constants. It is defined as induced polarization in direction 3 per unit applied stress, also applied in direction 3. d_{31} applies when the charge is collected from the same surface as with d_{33} , but the force is applied at right angles to the polarization axis.

$$d_{33} \approx -2.5 \cdot d_{31}$$



✓ Example: A poled PZT piezoelectric ceramic disk (length $l_0 = 2$ mm and poled in direction 3 has $d_{33} = 289$ pC/N, and its dielectric constant is 1300.

- What is the voltage applied across the thickness of this material if the electric field (E) is 250 kV/m?
- How much strain (x) will this voltage generate along direction 3?
- What will be the increase in length, in micrometers?

dielectric constant is the ratio of the permittivity of a material to that of a vacuum

$$\epsilon_r = \frac{\epsilon}{\epsilon_0}$$

Therefore, $\epsilon = 1300 \times 8.85 \times 10^{-12} = 1.15 \times 10^{-8}$ F/m

Because the initial length of the material is 2 mm, the voltage applied to the material would be

$$250 \times 10^3 \times 2 \times 10^{-3} = 500 \text{ V}$$

The strain generated in direction 3 by applying an electric field of 250 kV/m in the same direction will be given by

$$x = d_{33} \times E_3 = 289 \times 10^{-12} \times 250 \times 10^3$$

$$\Rightarrow x = 7.225 \times 10^{-5}$$

$$x = \frac{\Delta l}{l_0} = \frac{\Delta l}{2 \times 10^{-3}} \Rightarrow \boxed{\Delta l = 0.145 \mu\text{m}}$$

Thus, applying a voltage of 500 V to this cylinder of height 2 mm will cause an elongation of 0.145 μm .

Ferroelectric Domains

Consider a ferroelectric crystal (such as barium titanate in the tetragonal phase) in which the spontaneous polarization may be either up or down the c axis of the crystal. The cooperative displacement of the ions of several unit cells occurs during the formation of tetragonal BaTiO_3 from its cubic phase. This leads to the spontaneous formation of a region consisting of several unit cells, with all the unit cells' dipole moments lined up in the same direction. The region in which the polarization is in a given direction, is known as *ferroelectric domain*.

Ferroelectric domains are regions within a ferroelectric material, like barium titanate (BaTiO_3) in its tetragonal phase, where the spontaneous electric polarization of several unit cells aligns uniformly in one direction, either "up" or "down" along the crystal's c -axis. This alignment happens because of a cooperative displacement of ions in each unit cell, resulting in a net dipole moment across the region.

In the case of BaTiO_3 , the crystal structure changes from cubic to tetragonal at a certain temperature, causing each unit cell to develop a dipole moment due to the displacement of ions. These aligned regions, where the electric polarization is uniform, are what we refer to as ferroelectric domains. Domains can form as a way for the material to reduce its overall electrostatic energy, and adjacent domains may have opposite polarization directions to further minimize energy.

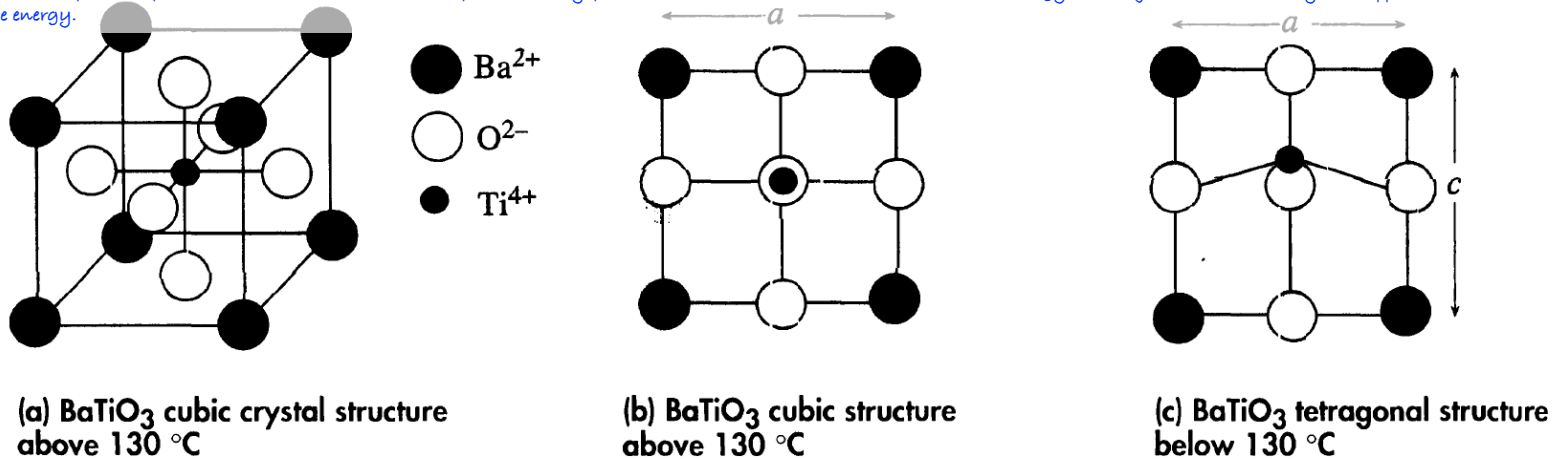
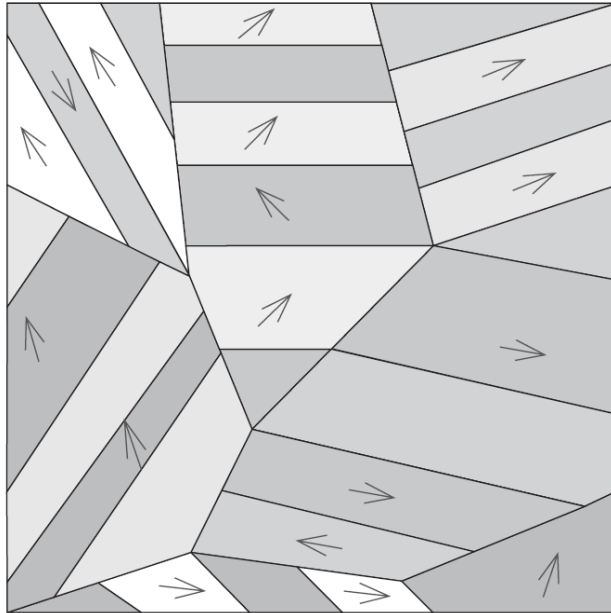


Figure 7.44 BaTiO_3 has different crystal structures above and below 130 °C that lead to different dielectric properties.

Is there only one domain in the ferroelectric crystal?

Ferroelectric domain in one part of a material cannot continue indefinitely because the process will gradually increase the free energy of the system. The growth of a ferroelectric domain will stop when it reaches a certain size. The total polarization in this domain will be compensated for by another domain next to it, in which the polarization is in the opposite direction. Thus, a ferroelectric material is comprised of many polar regions, in which each region has polarization in a certain direction. Domain walls in ferroelectrics are very thin boundaries (just a few angstroms) that separate domains polarized in different directions.



In absence of electric field, the polarizations associated with the different regions cancel each other out, and the ferroelectric material has no net polarization.

Randomly arranged ferroelectric domains in an unpoled ferroelectric.

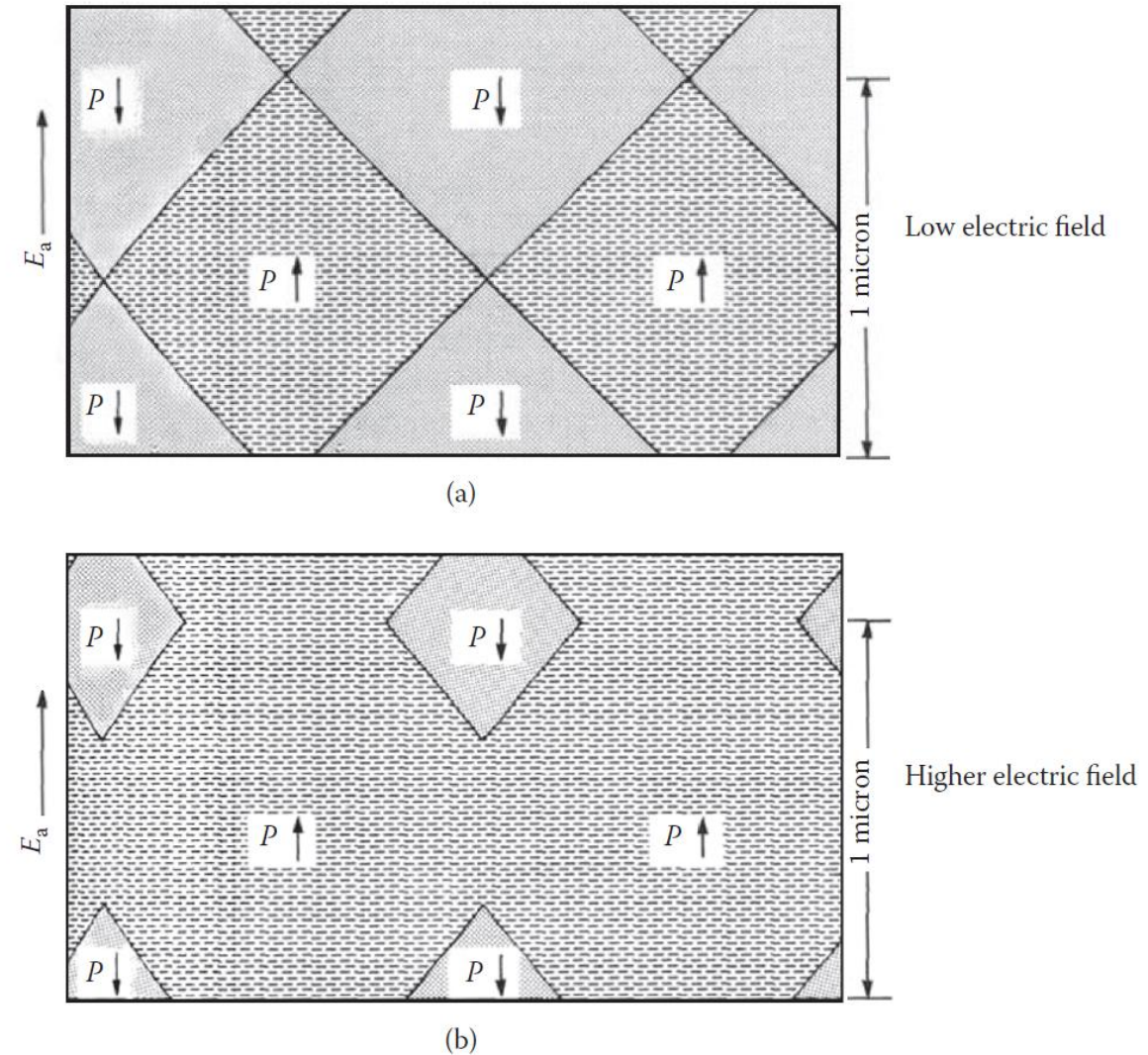
When an electric field is applied to a ferroelectric material, its domains begin to align with the electric field, and the material develops a net polarization. This is similar to the alignment of permanent dipoles in a polar material.

The application of an electric field helps to align the domains. This development of polarization in a ferroelectric material is nonlinear. This is a very important distinction between a linear dielectric material, such as silica (SiO_2), alumina (Al_2O_3), or titanium oxide (TiO_2) which shows only nonferroelectric polarization, and a nonlinear dielectric material such as the tetragonal form of BaTiO_3 .

$$P = \chi \epsilon_0 E$$

Not for ferroelectric materials

This equation which is applicable to linear dielectrics, cannot be used to describe polarization as a function of the electric field in ferroelectric materials.



Ferroelectric material under E field

The dielectric constant of ferroelectric materials is dependent on the strength of the electric field (E) applied. When the electric fields applied are relatively high, the entire material can become a single-domain structure. The material cannot generate any more ferroelectric polarization. This state of maximum possible ferroelectric polarization is known as the saturation polarization (P_s). The only small increase that is possible beyond P_s is due to the continued ionic and electronic polarization of the atoms or ions that make up a given ferroelectric material. The process of applying an electric field in order to align a substantial fraction of domains is known as *poling*.

E field needed for poling a ferroelectric material depends upon the field that is needed to move the domain walls. In practice, the poling process is often conducted in an insulating oil bath maintained at a high temperature, but below T_c . The higher temperature makes it possible to carry out poling at lower electrical fields because of increased domain wall mobility. The insulating oil bath prevents any arcing that may occur between the electrodes applied on the material being poled.

However, if an already poled piezoelectric is again exposed to high temperatures, it can also depole. *Depoling* means that the domains undergo randomization, which can cause the net piezoelectric effect to diminish or disappear. A general rule of thumb for using piezoelectrics is that they can be safely used up to a temperature of $\frac{1}{2}T_c$ without significant degradation of the piezoelectric activity. Another factor to consider is whether there are any potential changes in the crystal structure, even though the material will not become paraelectric.

Even at room temperature, domains in a freshly poled piezoelectric in time undergo some level of randomization after the poling electric field has been removed. This process is known as *aging*, and causes a decrease in the piezoelectric properties. The effects of aging on dielectric properties are usually logarithmic with respect to time and are accelerated at higher temperatures.

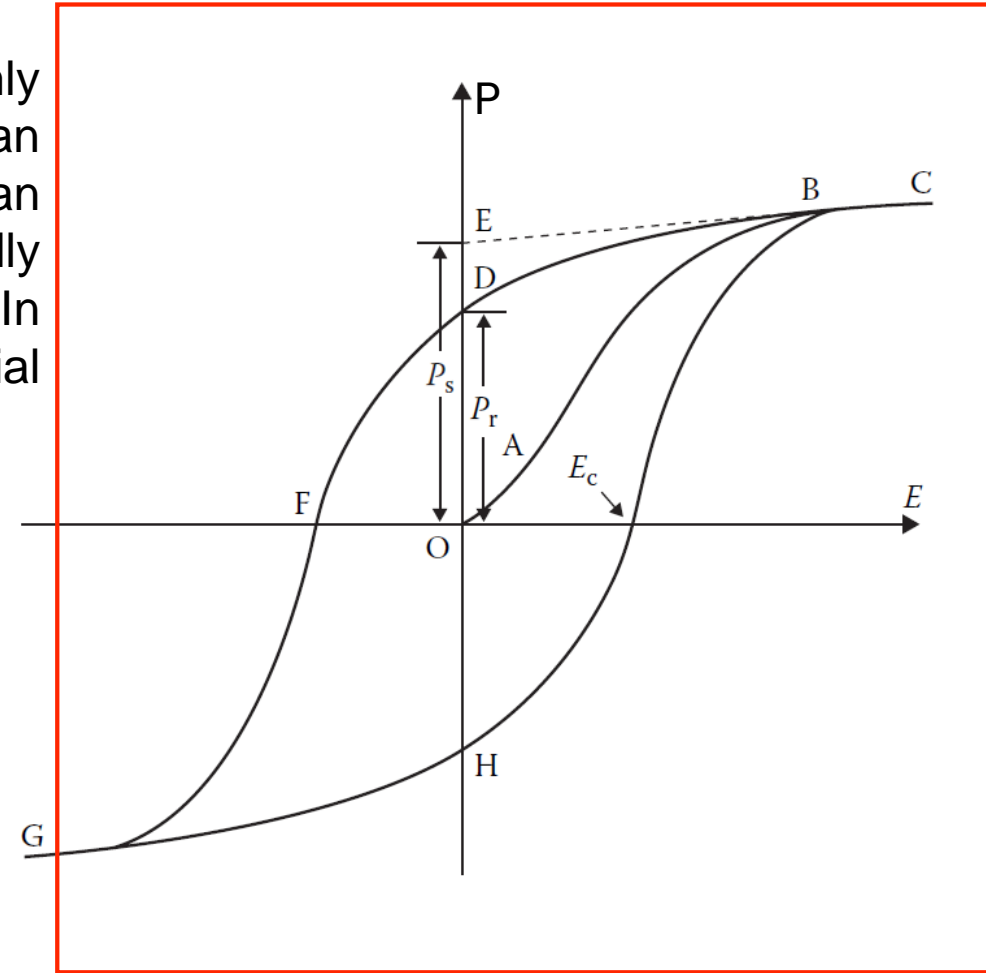
When the electric field is taken off, not all of the domains will return to their original random states of polarization. As a result, the ferroelectric material shows *remnant polarization* (P_r). We need to apply a magnitude equivalent in the opposite direction known as the *coercive field* (E_c) in order to bring the polarization back to zero by again randomizing all the domains. The trace of polarization (P) as a function of the electric field is known as the polarization–electric field (P – E) *hysteresis loop*.

Ferroelectric hysteresis loop

For an unpoled sample, the ferroelectric domains are at first randomly aligned. The starting point is the origin (O), where there is neither an applied electric field nor the development of net polarization. As an electric field is applied, a very small part of the hysteresis loop initially exhibits a polarization that is linear with the applied electric field. In this region, between points O and A, the ferroelectric material essentially behaves similarly to a linear dielectric.

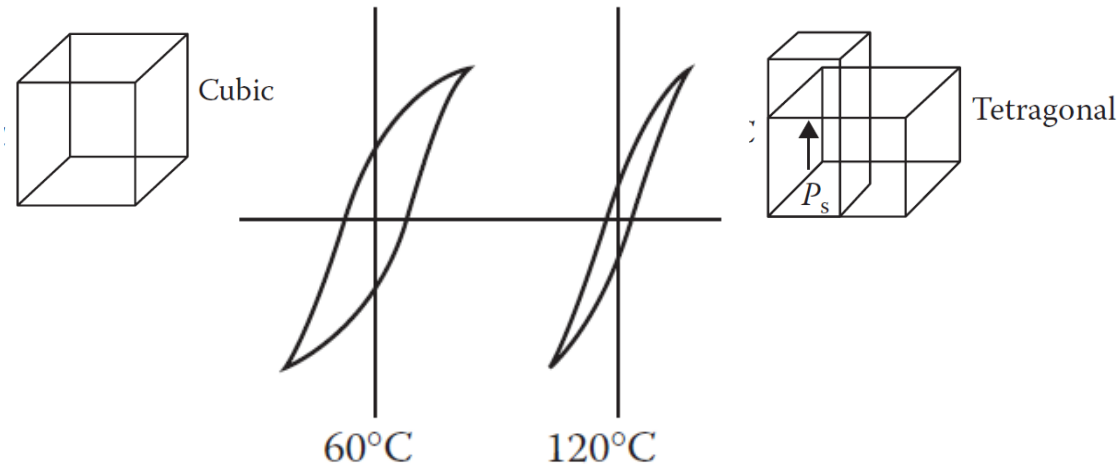
As we increase the field, the ferroelectric domains begin to realign. The realignment of ferroelectric domains between points A and B results in the development of relatively large polarization. As we reach point B, almost all the domains are aligned. The polarization value corresponding to point B is known as the saturation polarization (P_s). This is the maximum polarization in a ferroelectric material, ignoring the small effects of electronic and ionic polarizations that can continue to occur at high electric fields. Note that the slope of the region between points B and C is rather small. Thus, the dielectric constant of a ferroelectric at high electric fields is again rather small.

As the field decreases from point C toward point B and toward point D, some domains are able to switch their polarization directions and others are not. Thus, overall polarization decreases. However, a fraction of the domains continues to remain aligned with the direction of the field applied. This causes the ferroelectric material to develop a remnant polarization (P_r). To remove this P_r we must apply an electric field in a direction opposite to the original direction. The E field at point F is known as the coercive field (E_c), which is the field required to force all the domains back to a random configuration (zero polarization).



In general, the saturation polarization, which is the maximum polarization that can be obtained from a given composition of a ferroelectric material, is *not* a strong micro structure dependent quantity. However, the coercive field is very much a microstructure-sensitive property.

The appearance of the ferroelectric loop and the associated values undergo changes with temperature and especially depend on the particular crystal structure of the phases. For example, for BaTiO_3 , one of the phase transformations is that of a ferroelectric tetragonal structure changing to the paraelectric cubic structure at $T_c = 130^\circ\text{C}$



Origin of the pyroelectric effect

If the temperature is constant ($dT/dt = 0$) and the electrodes on this pyroelectric BaTiO₃ sample are connected to an ammeter, no current will flow through the sample because no free charges are left behind on the surfaces. If the temperature is increased ($dT/dt > 0$), the dipole moment for the ferroelectric material decreases. This means that the total polarization (P) decreases. So, the total bound charge density on the surfaces of the ferroelectric material also decreases. This means there will be now free charges on the surfaces of the pyroelectric material. The negative charges (i.e., electrons) flow from the top surface toward the ammeter, while a current (pyroelectric current) would flow in the opposite direction.

If we further cool the sample (i.e., $dT/dt < 0$), the ferroelectric polarization will increase. This will cause an increase in the bound charge density, and electrons will flow from the wire toward the pyroelectric material surface in order to compensate for the increased bound charge density.

